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A Continued Study of Optical Sound Generation and Amplification

Henry E. Bass and F. Douglas Shields

Physical Acoustics Research Laboratory
University of Mississippi
University, MS 38677
PARGUM 89-06

THE UNIVERSITY OF MISSISSIPPI
PHYSICAL ACOUSTICS RESEARCH GROUP
DEPARTMENT OF PHYSICS AND ASTRONOMY

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The general thrust of the research described in this report is acoustics of systems far from equilibrium. This topic is subdivided into sound amplification and sound generation though the two are very much intertwined. In the case of sound amplification, research is focussed on the propagation of sound through a gas which has internal states far from equilibrium. Sound generation as discussed in this report results from depositing energy in an internal state.

Calculations show that some very stringent conditions must be met if sound amplification is to be experimentally observed. For the magnitude of the gain to be appreciable, the v-t relaxation time can only be about one order of magnitude longer than the sound period. A number of experimental configurations were tried to meet these conditions. The effect was observed and measured in N_2/H_2, N_2/He, N_2/H_2O, and N_2/CH_4 mixtures.

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19. /Although the basic principles governing optoacoustic generation of sound have been well established for many years, the goal of the work reported here was to use this technique to study energy transfer at the molecular level. This required that all factors influencing the acoustic waveform including vaporization be accurately considered.

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Table of Contents

ABSTRACT

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A CONTINUED STUDY OF OPTICAL SOUND GENERATION AND AMPLIFICATION

1.0 BACKGROUND

The University of Mississippi's Study of Sound Generation and Amplification began in 1981 as ONR Contract N00014-81-0691. During the first 30 month period, the project involved Henry E. Bass, Lawrence A. Crum, and F. Douglas Shields as co-principal investigators. The first contract involved a shift in direction by the three principal investigators. Studies of momentum and energy accommodation at solid surfaces and ONR supported work in cavitation were brought to an orderly conclusion during the first 30 month period. Beginning in January of 1984, ONR Contract N00014-84-C-0193 extended the Study of Optical Sound Generation and Amplification for an additional three-year period under the direction of Henry E. Bass and F. Douglas Shields. A summary of research accomplished during the first 66 months of the study was reported in PARGUM 87-01 issued at the end of the contract period.

ONR awarded a new three year contract for A Continued Study of Optical Sound Generation and Amplification beginning 1 January 1987. This final report presents a summary of research performed during this final three-year period as well as a summary of major findings since the inception of this project. For the most part, research results have been reported in the open literature or technical reports. The reader is referred to these publications for details. This report will deal with the general direction of research and the most significant results.

A major product of university based research is the training of graduate students. A list of graduate students who received a major fraction of their support from this contract is included in section 5.0.

The general thrust of the research described in this report is acoustics of systems far from equilibrium. This topic is subdivided into sound amplification and sound generation though the two are very much intertwined. In the case of sound amplification, research is focussed on the propagation of sound through a gas which has internal states far from equilibrium. Sound generation, as discussed here, results from depositing energy in an internal state.

Theoretical studies by Bass and Bauer[1] showed some years ago that a sound wave should be amplified upon passage through a gas with an overpopulation of vibrationally excited states. They named this effect SACER (Sound Amplification from Controlled Excitation Reactions) due to similarity to the LASER.

Based upon the work of Gilbert,[2] Bass chose to experimentally study amplification associated with chemical reactions. The system chosen for study was H_2/Cl_2 mixtures. The energy transfer rate constants required to predict amplification were measured independently and published in 1984.[3] Actual amplification was observed in 1983. These observations were published in 1985.[4]

Basically, the phenomenon observed by Bass and Detsch (a former Ph.D. student now at NCSC) can be described as follows. A UV lamp was used to photodissociate Cl_2. The resulting Cl atoms react very rapidly and exothermically to produce HCl. The rate of reaction depends upon the local pressure and temperature. Since the reaction is exothermic, and increase in reaction rate gives rise to a relative local increase in temperature; that is, local temperature and pressure variations are amplified.

Although the chemical SACER did exhibit gain, difficulties associated with controlling the chemical reaction and the complexity of the reaction scheme led us to abandon this effort in 1983 in favor of a system based solely on vibrational energy transfer in the gas. This approach entitled "Propagation of sound through gases with an over-population of vibrationally excited states" was being pursued simultaneously by Shields.

His theoretical work published in 1984[5] indicated that amplification should be observed following an electrical discharge in N_2/He or N_2/H_2 mixtures. This approach proved to be quite successful.

Calculations showed that some very stringent conditions had to be met if sound amplification was to be experimentally observed. For the magnitude of the gain to be appreciable, the v-t relaxation time could only be about one order of magnitude longer than the sound period. A number of experimental configurations were tried to meet these conditions. Suffice it to say here that the effect was observed and measured in N_2/H_2, N_2/He, N_2/H_2O and N_2/CH_4 mixtures.

In the process of making these measurements, the variation of the sound velocity in the gas as the vibrational energy decayed into translation were measured and from these measurements the variation of the translational temperature during the relaxation process was determined. This, in turn, allowed a determination of the vibrational temperature as a function of time and, thus, the vibrational relaxation time and its temperature dependence. In the diatomic gases studied (N_2 and CO), these numbers are very difficult to measure otherwise and constitute a valuable addition to the literature.

While pursuing the problem of sound amplification in an excited gas, work was also underway investigating sound generation. The approach taken was the classic spectrophone. When a fluid is subjected to pulses of electromagnetic radiation of the proper wavelength, absorbed energy causes the gas to heat and expand resulting in a measurable acoustic impulse. Although the basic principles governing the spectrophone have been well established for many years,[6] it was our goal to use this technique to study energy transfer at the molecular level. This required that other factors influencing the acoustic waveform were accurately described.

Although our long-term goal was to examine dynamics in liquids, the first system studied under the previous contract was gaseous CO_2. The gas phase was chosen to give

3

experimental control of the rate of energy transfer processes by varying the pressure. CO_2 was chosen because it weakly absorbed radiation from an existing CO_2 laser. Results of this effort were published in 1983.[7] That publication includes the first comprehensive theoretical treatment of the optoacoustic effect in a weakly absorbing (nearly transparent) fluid.

Optoacoustic studies in liquids typically involve a very short optical penetration depth. A gaseous analog to this situation is SF_6, absorbing 10.6 m radiation from a CO_2 laser. A thorough study of this system was begun in 1983 and was completed in 1986.

One effect of optical absorption is that the laser beam decreases in amplitude as it penetrates the fluid. Since the acoustic pressure generated is proportional to the incident optical intensity, the acoustic pressure is not cylindrical but, instead, it appears as an exponential decay rotated about the laser beam path. Since the acoustic pressure is greater near the optical entry point, in addition to the cylindrically spreading wave (assumed for CO_2), there is an acoustic wave which propagates in the direction of the laser beam.

Optoacoustic studies of SF_6 excited with a CO_2 laser were undertaken to investigate the effect of strong optical absorption. This work, published as Ref. 8, showed a very interesting effect in addition to including the first successful technique for predicting the optoacoustic signal in the presence of strong optical absorption. Specifically, it was found that as the gas pressure decreased, the acoustic overpressure steadily decreased until a pressure of about 200 mtorr was reached. Near 200 mtorr, the acoustic overpressure went through zero and became negative. That is, absorption of optical energy resulted in net cooling of the gas!

At first glance (and even second), cooling of the gas as a result of energy deposition appears to violate several, if not all, the laws of thermodynamics. Microscopically, this effect can be understood as follows. When radiation is absorbed by SF_6, some molecules are excited from the ground state to the $n_3 = 1$ state. The $n_3 = 1$ state is closely coupled to the $n_4 + n_6 = 1$ state which is slightly higher in energy. At high pressure, during a few

4

collisions molecules in the $n_3 = 1$ state transfer to the $n_4 + n_6 = 1$ state with the additional energy required coming from translation (the gas first cools). As energy is transferred down the manifold of vibrational states in subsequent collisions, the gas heats. At low pressures, however, collisions at the container walls become more frequent. At about 200 mtorr, the $n_3 = 1$ to $n_4 + n_6 = 1$ transfer is more probable than a wall collision (the gas cools), but transfer of $n_4 + n_6 = 1$ to the walls is more probable than transfer down through the manifold of vibrational states (there is no subsequent heating). The excess energy is carried off by the cell walls (heat sink). A set of energy transfer rate constants which predict the high pressure optoacoustic signal in SF_6 reliably predicts the transition from heating to cooling.

Although these results in SF_6 left us excited as well as confused, we could not imagine an encore performance. All work on the gas phase was discontinued in 1984. Fortified with the excellent agreement between theory and experiment in the gas phase, measurements in liquids began in earnest in 1984.

There are numerous publications reporting optoacoustic measurements in fluids. By and large, these papers are concerned with the amplitude of the optoacoustic signal in different fluids or with differing laser beam geometries. Our goal was to use optoacoustics as a tool to study the molecular processes which give rise to the acoustic signal then optimize the acoustic amplitude.

The basic problem associated with quantifying molecular dynamics in the liquid state is that such processes are extremely fast and there is no experimental parameter (such as pressure) to slow these processes down. The speed of the process to be studied placed severe (perhaps insurmountable) constraints on our experimental system. The best time resolution published as of 1984 was that achieved by Sullivan and Tam.[9] Our initial strategy was to reproduce the results of Sullivan and Tam and then improve temporal resolution.

An optoacoustic signal in propanol was first observed in our laboratory in the fall of 1985. By the fall of 1986, the basic results of Ref. 9 had been reproduced in propanol with a red dye and other alcohols. In addition, using a broadband hydrophone, the absolute magnitude of the optoacoustic signal was found to agree well with theoretical predictions. The decrease in optoacoustic amplitude with distance from the excitation zone was also found to agree with theory. Measurements were also made of the optoacoustic amplitude for different optical penetration depths and input energies. Each observation agreed well with theory.

At the end of 1986, we were comfortable with the technique to measure very rapid conversion of electromagnetic radiation into an acoustic pulse. The next goal was to improve temporal resolution so that microscopic molecular transfer times could be determined. An alternative to improved temporal resolution was selection of a fluid which relaxes more slowly than propanol or water. Ultimately, this was the direction pursued. The fluid chosen was CS_2.

The foregoing was meant to provide the reader background for the most recent contract period and some rationale for the approaches taken. Accomplishments during the most recent three-year period are reported in the following two sections: one devoted to Propagation of Sound Through a Gas with an Overpopulation of Vibrationally Excited States and one devoted to Optoacoustic Studies of Liquids.

2.0 OPTOACOUSTIC STUDIES OF LIQUIDS

2.1 Introduction

Investigations of optoacoustic generation in liquids are well documented.[6,8,9] Most of these studies were carried out using low optical energies and small optical absorption

coefficients. A small optical absorption coefficient makes the symmetry of the problem simple, the mathematics tractable. In the low optical energy regime, the acoustic generation mechanism is thermal expansion. This is the basis for linear optoacoustic theory. Nonlinear effects occur when the liquid experiences multiphoton absorption or a phase transition.

On a molecular level, the optoacoustic effect can be broken down into several different steps. The process of converting optical energy to acoustical energy begins with the absorption of photons by the molecules of the fluid. This absorption leaves the molecules in an excited state. In the present case, a nitrogen laser used as the energy source produces electronic excitation of the molecules. Dissipation of this energy can occur through several mechanisms including photochemical processes, radiative decay, and nonradiative decay. In nonradiative decay, the electronic excitation energy is transferred to translational, rotational, or vibrational states of the molecule. Through interactions with other molecules this rotational and vibrational energy can be converted into translational energy creating a temperature rise in the fluid. In our experiment, following each pulse from the laser, the fluid is allowed to cool to an ambient temperature. This alternate heating and cooling creates a pressure variation which is observed as acoustic pulses.

The process of energy transfer and the rate at which it occurs varies from one liquid to another because the energy levels and rate of energy transfer depend on the structure of the molecules. If the rate of production of translational energy is slow due to internal relaxation processes, the shape of the acoustic pulse should be governed by these relaxation processes. The experimental system must be capable of resolving very short acoustic pulses in order to resolve events occurring on this time scale. Otherwise, the pressure profile is dominated by geometrical factors of the experiment.

We chose to study carbon disulfide (CS_2) because previous ultrasonic absorption measurements[10] have already shown that the transfer of energy between translational and vibrational states is relatively slow (compared, for example, to H_2O). Mr. Charles

7

Thompson completed his M.S. work in December of 1987, which was a study of energy transfer in CS_2. His thesis was issued as a Technical Report and published in the Journal of the Acoustical Society of America.[11]

2.2 Experimental Configuration and Results

The experimential setup will be described here for completeness even though a similar description has been provided in previous reports.

A block description of the experimental technique is shown in Figure 1.1. This technique utilizes two lasers. A 1.25 MW nitrogen laser emitting 800 ps pulses in the UV (337 nm) is used as the optoacoustic source. A 3 MW continuous He-Ne laser runs parallel to the excitation zone. It is then focused on a photodiode which is coupled to a digitizing oscilloscope. The probe laser responds to refractive index gradients which are produced as a result of the acoustic wave. These gradients cause small deflections of the probe beam which are detected by the photodiode. The observed signal is proportional to the pressure gradient.
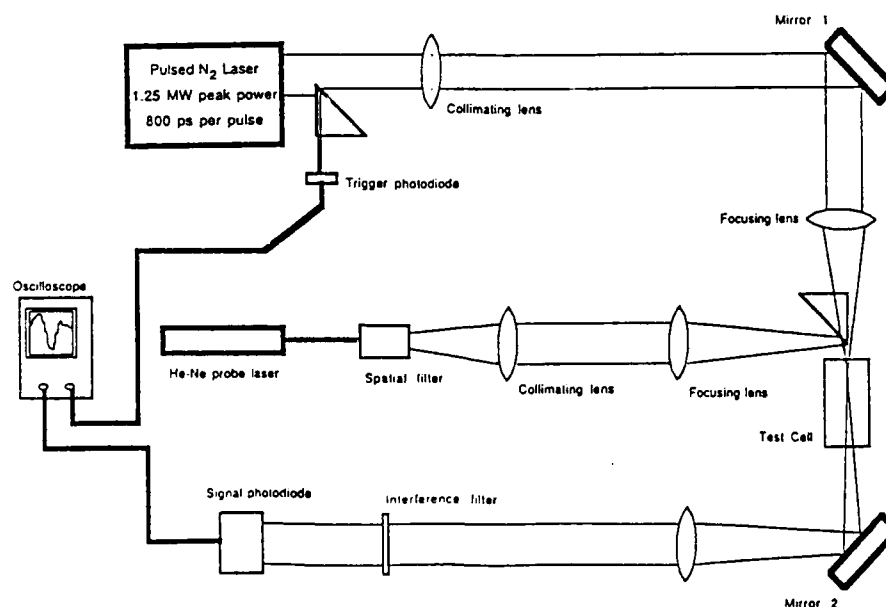

Fig. 1.1 Experimental Apparatus

This experimental configuration was used to quantitatively compare measured and predicted optoacoustic amplitude as functions of input energy, distance between excitation zone and probe beam, thermal expansion coefficient of the liquid, optical absorption coefficient of the fluid, specific heat of the liquid, and excitation beam properties. So long as the input energy density is small, experimental and theoretical results compared quite well. A detailed description of the comparison is given in the preprint attached as Appendix A which has been submitted to the Journal of the Acoustical Society of America. Appendices A and B are taken in large part from Stanley Cheyne's Ph.D. dissertation which was issued as a Technical Report (PARGUM 89-01).

2.3 Interpretation of Optoacoustics in Fluids

At the UV wavelengths employed in this experiment, the laser photons which are absorbed result in electronic excitation of the recipient molecules. This electronic energy is then rapidly converted to vibrational and translational energy which is manifested macroscopically as thermal expansion. We conclude that the electronic excitation does not lead directly to thermal expansion by comparison of the UV results to measurements using IR lasers. The IR lasers produce photons with insufficient energy to cause electronic excitation, yet the efficiency at which the electromagnetic energy is converted to thermal expansion is identical to that for the UV measurements (at least in the linear regime). Since the observed thermal expansion depends only upon the total energy deposited in the fluid and not on the optical wavelength, we conclude that it is vibrational and/or translational modes which give rise to expansion.

Further insight into the critical energy flow path can be gained from Thompson's[11] results. Specifically, in the case of CS_2, he found that following deposition of energy by the laser, there was a time lag for resultant thermal expansion of about 90 nsec which

seemed to be associated with transfer of energy from an electronic (initial) state to translation (or vibration) as well as a time constant of 1.5 nsec for vibrational relaxation. These results indicate that when energy is added to the fluid, that energy must undergo internal conversion processes prior to causing thermal expansion. Further, since the laser used has a pulse length of 0.8 nsec, essentially all the laser energy deposited resides in internal states at the end of the pulse.

The observation that deposited energy resides in excited states for relatively long time periods gives rise to some interesting consequences. Specifically, for a large energy flux, this raises the possibility of depositing photons in a grouping of molecules more rapidly than the energy is redistributed in the fluid.

Refer to Figure 1.2. Up to an input energy of about 20 μJ, the optoacoustic signal strength varies linearly with input energy. A transition occurs at about 20 μJ where the amplitude again increases linearly but with a greater slope. At about 80 μJ, the optoacoustic amplitude begins to vary nonlinearly with input laser pulse energy.
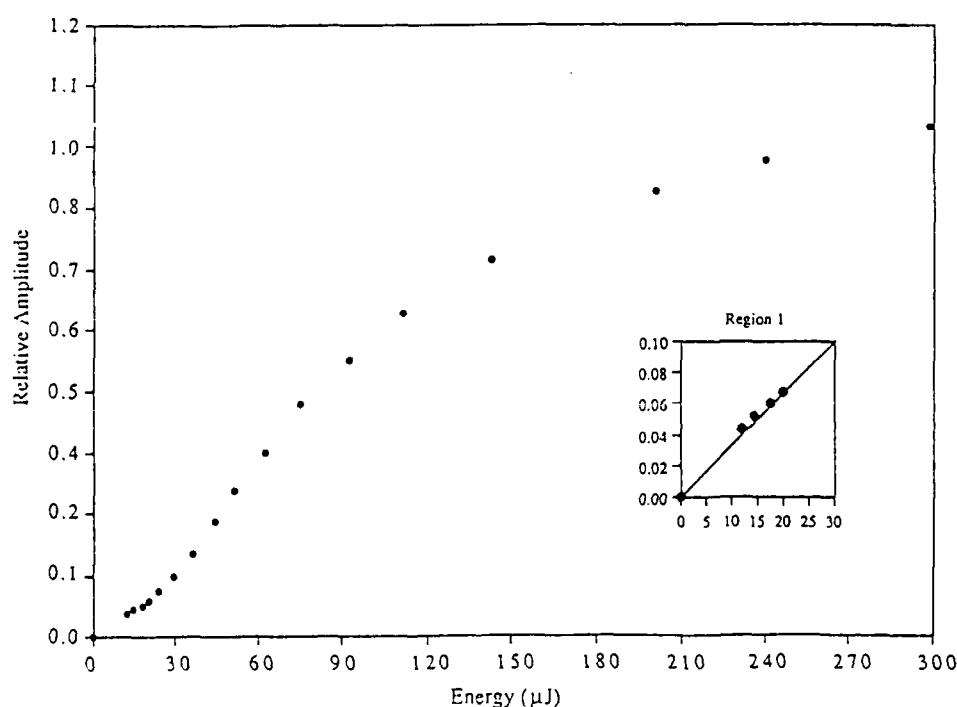

Fig. 1.2

10

The interpretation of these changes in slope is discussed in the preprint attached as Appendix B which has also been submitted to the Journal of the Acoustical Society of America. In summary, we found that the first change in slope occurs when the energy density is sufficiently high to cause the fluid to undergo a transition to the vapor phase. Initially, only fluid at the beam center is vaporized but as the energy increases, a larger percentage of the focal volume is vaporized. This means that the parameters which predict optoacoustic amplitude change from liquid to gas values. At the second change, the energy density is sufficient to cause all the fluid in the excitation volume to vaporize so the excitation volume behaves as a gas. Near this energy level, visible bubbles are noted. The fact that this transition proceeds in a smooth and predictable manner suggests that the microscopic processes which lead to cluster disintegration are rate limited by the electronics to translational energy transfer step.

Based upon the research to date, we feel that we can describe the transfer of energy from excited electronic states to translation and the phase transition from liquid to gas. There is still much to be learned. Specifically, this technique for measuring relaxation times in liquids should be extended to include mixtures. Due to inherent limitations on time resolution of the apparatus, such measurements will probably be possible only for CS_2 mixtures. By measuring relaxation time as a function of additive concentration, one should be able to determine what differences (if any) there are between liquid and gas phase intermolecular transfer of energy. Another promising avenue of study is to examine the optoacoustic waveform near the freezing point. One would expect clusters to grow near freezing thus slowing the relaxation processes observed.

The research program in optoacoustic studies of liquids at the University of Mississippi will terminate with this contract period. It is our hope that other investigators will pursue this very promising research activity. Although optoacoustics has developed into a practical tool for studying material properties, there is still a great deal to be learned about the time evolution of the optoacoustic signals.

3.0 PROPAGATION OF SOUND IN VIBRATIONALLY EXCITED GASES
(SACER)

3.1 Introduction

This project was begun several years ago as a search for SACER (Sound Amplification from Controlled Excitation Reactions). The effect has been observed in N_2 with added amounts of He, H_2, H_2O and CH_4 and the measured amplification found to exceed theoretically predicted values. In the process, the experimental procedure has enabled the measurement of some here-to-fore difficult-to-observe relaxation times and their temperature dependence.[12,13]

The experimental method has been described in earlier reports. It involves exciting the vibrational states in a gas with an electrical discharge and observing the change in velocity and absorption of sound in the gas over a period of a few tens of milliseconds following the discharge. In N_2 and a few other selected gases most of the electrical discharge energy winds up in molecular vibrational energy in a few microseconds. By measuring the energy the discharge dumps into the gas, we have estimated the vibrational temperature immediately following the discharge. Vibrational temperatures 1000 to 2000 K above translational temperatures are obtained in this way.

Translational temperatures are determined from the sound velocity which, in turn, is determined from the resonant frequency of the discharge tube which changes with time following the discharge. The sound velocity in this way becomes a thermometer able to sense the gas temperature changes on a millisecond time scale, and the discharge tube a kind of spectrophone that measures the rate of conversion of vibrational energy into translational energy.

12

Our recent work has been concerned with carbon monoxide. This gas was chosen because calculations from electron collision cross sections showed that it could also be excited vibrationally by an electrical discharge. It was expected to behave in a way similar to N_2 but to have the additional property of being infrared active. We, therefore, expected to be able to observe the decay of the vibrational temperature directly from the emitted infrared. (In N_2 this decay was only inferred from the resulting rise and fall of the translational temperature). Unfortunately, as it turned out we were not able to get enough of the discharge energy deposited in the pure CO to sufficiently raise its vibrational temperature to observe SACER. However, we were able to add small quantities of CO to N_2 and H_2 and use its emission to monitor the vibrational temperature in these gases. Tim Ruppel reported this work in his Master's Thesis which was issued as an ONR Technical Report (PARGUM 89-02). That research has also been written up for publication in the Journal of the Acoustical Society of America. A preprint is attached as Appendix C.

3.2 Work During the Past Year

During the past year we have completed this work on N_2/CO, H_2/CO, and H_2/He/CO mixtures. As discussed above, the radiation from CO when added in small quantities can be used to monitor the decay of vibrational energy in the mixture. In the case of N_2 and CO, there is vibrational coupling between the first level in each gas. With CO and H_2 the second CO level is in very close resonance with the first H_2 level. In both cases the v-v exchange is enough faster than v-t to allow the CO vibration to remain in equilibrium with either the N_2 or the H_2 vibration.

In the case of N_2 the relaxation was slow enough that the actual vibrational temperature could be plotted as a function of time. Very satisfactory agreement was obtained between values measured in this way and values inferred from translational

13

temperature curves. These measurements also subtantiated the equation we had previously devloped for the ratio of the conduction time of vibrational energy to the conduction time of translational energy. This equation given in Ref. 13 (Eq. (4)) is

$$\frac{\tau_{vc}}{\tau_{tc}} = 1 + \frac{9}{4}\frac{R}{C_{tr}}.$$

Few measurements of this ratio have been reported and the development and test of this equation should be a useful contribution.

The measurements in H_2 showed that this gas relaxed so fast that we were not able to observe SACER. However, by adding He, the relaxation rate was slowed and we were able to determine relaxation times and their temperature dependence in H_2 and mixtures of H_2 and He. These rates are very difficult to determine by other means because the large spacing of the vibrational energy levels in H_2 make it difficult to get much energy into vibration. In our experiment, the needed high vibrational temperatures were obtained without a corresponding elevation of translational temperature.

3.3 Future Work

The experimental technique developed in this work enables the measurement of sound velocities and absorption in gases when the temperature is changing on a scale only an order of magintude larger than the sound period. This technique will likely find other applications in experiments involving gases that are not in thermal equilibrium. However, the gases that can be vibrationally excited by an electrical discharge are limited. We have no plans at present to continue the study of SACER in gases with this equipment.

14

4.0 SUMMARY AND CONCLUSIONS

Major results of this research program are:

1. Experimental verification of sound amplification in a chemically reacting mixture [JASA 75 (1984) and JASA 77 (1985)].

2. Observation of kinetic cooling of a gas following irradiation by a laser pulse [JASA 74 (1983) and IEEE UFFC-33 (1986)].

3. Measurement of vibrational relaxation time of a liquid using a pulsed spectrophone [JASA 85 (1989)].

4. Observation and explanation of nonlinear optoacoustic amplitude in a strongly absorbing fluid [JASA (to be published, preprint attached)].

5. Theoretical prediction of amplification of an acoustic signal in a gas following electrical discharge and subsequent observation [JASA 76 (1984) and JASA 81 (1987)].

6. Use of acoustic amplification to measure temperature dependence of vibrational relaxation times [JASA 81 (1987), JASA 83 (1988) and JASA (to be published (1990)].

7. Calculation and measurement of ratio of vibrational thermal conductivity to translational thermal conductivity in gases [JASA 83, (1988)].

8. Use of infrared emission following an electrical discharge to measure decay of vibrational temperature in a gas while the translational temperature change is being measured simultaneously acoustically [JASA (to be published (1990)].

This research program only begins to explore the nature of acoustics in media far from equilibrium. The inherently nonlinear nature of these general problems gives rise to mathematical difficulties but also lead to new and interesting effects.

5.0 SUMMARY OF GRADUATE STUDENTS

Degrees awarded with ONR support since start of project

1 July 1981

Student	Current Employment
Richard Detsch, Ph.D., 1983	Naval Costal Systems Center
David Young, M.S., 1983	Junior College Teacher
Gary Hansen, Ph.D., 1984	Science and Technology Corporation
Ron Roy, M.S., 1984	National Center for Physical Acoustics
Anthony Atchley, Ph.D, 1985	Naval Postgraduate School
Manaf Ali, Ph.D., 1985	Iraqi Attache to USSR
Dadang Iskandar, Ph.D., 1985	University Professor, Indonesia
Kerry Commander, Ph.D., 1985	Naval Coastal Systems Center
Bruce Layton, M.S., 1986	Junior College Teacher

Degrees awarded with ONR support during current contract period

Student	Current Employment
Charles Thompson, M.S., 1987	Naval Oceanographic Research and Development Activity
Stanley Cheyne, Ph.D., 1989	Georgia Tech. University
Timothy Ruppel, M.S., 1989	University of Mississippi (Ph.D. Candidate)
James Belcher	University of Mississippi (Ph.D. Candidate)

16

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APPENDIX A

19

A STUDY OF OPTOACOUSTIC SIGNAL AMPLITUDE IN WEAKLY ABSORBING FLUIDS

by

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ABSTRACT

The optoacoustic effect has been experimentally studied. These results have been compared to existing theoretical predictions based upon linear thermal expansion. The dependence of optoacoustic amplitude on the coefficient of thermal expansion, propagation distance, and laser pulse energy were measured. The experimental observations were found to be in agreement with theory. The signal amplitude was also measured as a function of optical absorption coefficient. It was found that the observed signal agreed with theory so long as the absorption coefficient was small. The absolute magnitude of the optoacoustic signal was also measured and compared to theory.

INTRODUCTION

There are several physical mechanisms involved in optically induced sound, or optoacoustics. This study concentrates only on the generation of acoustic waves by means of thermal expansion of a liquid following the absorption of a laser pulse. Theories of optoacoustics based upon the thermal expansion mechanism in weakly absorbing liquids have been developed and experimentally tested with reasonable success.[1-3] Sullivan and Tam[4] adopted the theory developed by Lai and Young[5] and experimentally studied the effects of excitation beam geometry. They found that short acoustic pulses could be produced by decreasing the beam waist of the excitation laser. This paper concentrates on the effects of other parameters involved in optoacoustic generation. Among these parameters are the laser pulse energy, coefficient of thermal expansion, propagation distance, and the optical absorption coefficient.

THEORY

The theoretical treatment of optoacoustics by the thermal expansion mechanism has been carried out by several authors.[5-7] We have adopted the theory developed by Lai and Young[5] neglecting any contributions from electrostriction which should be acceptable unless optical absorption is very small.[3] We begin with the wave equation

$$\left(\frac{1}{c^2} \frac{\partial^2}{\partial t^2} - \nabla^2 \right) p(r,t) = \frac{\alpha \beta}{C_p} \frac{\partial I(r,t)}{\partial t} \tag{1}$$

where c is the speed of sound, p is the acoustic pressure, α is the optical absorption coef-ficient, C_p is the specific heat, and I is the intensity distribution of the laser pulse. If we let

$$\left(\frac{1}{c^2} \frac{\partial^2}{\partial t^2} - \nabla^2 \right) \phi(r,t) = I(r,t) \tag{2}$$

where $\phi(r,t)$ is a velocity potential, then Eq. (1) becomes

$$p(r,t) = \frac{\alpha \beta}{C_p} \frac{\partial \phi(r,t)}{\partial t} . \tag{3}$$

If we use a Gaussian intensity distribution described by Lai and Young[5] as

$$I(r,t) = \frac{E}{2\pi^{3/2}} \frac{1}{R^2 \tau_p} \exp\left(-\frac{r^2}{2R^2} - \frac{t^2}{2\tau_p^2} \right), \tag{4}$$

then Eq. (3) has a solution

$$p(r,t) = \frac{\alpha \beta}{C_p} \frac{E}{8\pi^{1/2}} \left(\frac{c}{r} \right)^{1/2} \tau_e^{-3/2} \frac{d\phi_0(\xi)}{d\xi} \tag{5}$$

21

where

E =   laser pulse energy,

r =   acoustic propagation distance,

τ_e = $\left(\tau_p{}^2 + \tau_a{}^2\right)^{1/2}$,

τ_p =   time duration of laser pulse,

τ_a =   acoustic transit time,

t' =   retarded time $= t - \frac{r}{c}$,

R =   excitation beam radius, and

$$\Phi_0(\xi) = \sqrt{\frac{\pi}{c}} \, |\xi|^{1/2} \left[\frac{\sqrt{2}}{\pi} K_{1/4}\left(\frac{\xi^2}{4}\right) + 2\Theta(\xi) \, I_{1/4}\left(\frac{\xi^2}{4}\right) \exp\left(-\frac{\xi^2}{4}\right) \right].$$

Here,

ξ = $\left(t - \frac{r}{c}\right)/\tau_e$

Θ =   *Heaviside step function, and*

$K_{1/4}$ and $I_{1/4}$ are imaginary Bessel functions of 1/4 order.

Sullivan and Tam investigated the time dependence of $p(r,t)$ which depends upon τ_e, τ_p, τ_a, R and ξ. In the following, we will ignore the time dependent terms and examine the amplitude

$$A = \frac{\alpha\beta E}{C_p 8\pi^{1/2}} \left(\frac{c}{r}\right)^{1/2} \tau_e{}^{-3/2}. \tag{6}$$

Specifically, the effect of changing α, β, and E will be explored.

EXPERIMENT

The experimental configuration is patterned after Sullivan and Tam[4] and has been described in detail elsewhere.[8] The principle components consist of two lasers. A pulsed laser is used as a source and a continuous (cw) laser is used to detect the optoacoustic

22

signal. The experimental system is shown in Fig. 1. A nitrogen laser was used as the excitation source. It emitted 800 ps UV (337 nm) pulses with a maximum energy/pulse of 1 mJ. This gave a maximum peak power of 1.25 MW.

The UV pulse first encountered a right angle prism where a small percentage of the beam is reflected to the trigger photodiode. The major portion of the beam passes unperturbed to a fused silica collimating lens. Then, the pulse impinges on a small quartz test cell after passing through a focusing lens. Unless otherwise indicated, the test cell contained proponal doped with red dye.

The detection beam is a cw 3 mW Helium-Neon (HeNe) laser operating at a wavelength of 632.8 nm. First, it is spatially filtered and collimated to a diameter of about 1.5 cm. Then, it passes through a focusing lens (focal length = 35 cm), is reflected ninety degrees by a small silver-coated back-surfaced mirror (1 cm $\times$ 1 cm), and allowed to pass through the test cell. In the test cell, the probe beam is fixed parallel and above the excitation beam. Then, it passes through another lens which focuses the beam on a photodiode mounted on an X-Z translator. This lens can be moved along the beam path to vary the intensity on the signal photodiode. The probe beam is positioned by moving the photodiode until the same change in output is observed for equal positive or negative angular displacements.

The probe beam responds to changes in the optical index of refraction associated with the generated acoustic wave. As the density gradient traverses the probe laser beam, it causes the beam to deflect. This deflection is observed by monitoring the output of the photodiode. The output of the photodiode was amplified by a 100 kHz - 1.3 GHz bandwidth amplifier.

The laser pulse energy was varied by placing thin glass microslides (.23 mm thick) in the excitation beam path. The absorption provided as a function of the number of slides was determined with a pyroelectric detector. The precision of the energy meter is ± 2 μJ. The measured energy delivered to the test cell as a function of the number of slides is shown in Fig. 2. Figure 3 is a plot of optoacoustic signal amplitude vs laser pulse energy.

The linear relationship between A and E is in agreement with Eq. (6). This is expected as long as

$$\Delta T + T_o < T_b$$

where $\Delta T = \Delta E / C_p$, T_o = initial temperature, and T_b is the boiling temperature of the liquid. This condition was always met in this investigation. The slope of the straight line was found using a least squares fit to the experimental data. The error bar represents one standard deviation in the slope.

The next parameter affecting optoacoustic amplitude considered was the propagation distance r. Increasing the propagation distance of the acoustic wave was achieved by moving the excitation beam away from the probe beam. This was done by placing mirror M1 (see Fig. 1) in an optical mount and making rotational movements about the horizontal axis. The propagation time could be determined by monitoring the optoacoustic pulse on the oscilloscope. Knowing the sound velocity and the propagation time, the propagation distance could be calculated.

The results of this measurement are shown in Fig. 4. The reference propagation distance and amplitude are 1 mm and 1 mV, respectively. This graph shows that the decrease in signal amplitude is proportional to $1/\sqrt{r}$ which is characteristic of cylindrical spreading. The error bar represents one standard deviation from the straight line which is a least squares fit to a $1/\sqrt{r}$ dependence. The experimental results are considered to be in agreement with Eq. (6).

According to Eq. (6), the optoacoustic amplitude should be directly proportional to the coefficient of thermal expansion β. To test this dependence, liquids with different values of β were used. The input energy density was made constant by adding red dye to make the optical absorption coefficient of each test liquid the same. The results of these measurements are shown in Fig. 5. The error bar represents typical uncertainties in the

amplitude measured for propanol as determined in previous measurements. The linear relationship is in agreement with Eq. (6).

Another point of comparison is variation of signal strength with the optical absorption coefficient α. According to Eq. (6), the acoustic amplitude should vary linearly with α. This measurement involved adding red dye to propanol to increase α. The results are shown in Fig. 6. It is apparent that the simple description of the beam used to derive Eq. (6) is insufficient for large optical absorption.

As the probe beam propagates alongside the excitation beam, it undergoes a deflection which is a result of the sum of all the gradients in refractive index encountered in the fluid. The probe beam will be most sensitive to the index gradients near its focal plane if the gradients there are are confined to spatial dimensions on the order of the probe beam diameter. However, there will be some deflection due to density gradients all along the probe beam path. When the absorption coefficient is small (penetration depth large), much of the excitation beam passes entirely through the test cell. In this case, an increase in absorption coefficient does, indeed, give rise to an increased optoacoustic signal. Once the absorption coefficient is large enough to trap all the excitation energy within the test cell, further increases in the absorption coefficient have a much smaller effect. This is because the total optical energy within the test cell is now constant. As a result, the amplitude of the observed optoacoustic signal will remain constant. Again, the error bar represents typical uncertainties in previous propanol measurements.

The final measurement performed was an attempt to measure the absolute magnitude of the optoacoustic signal. This was done by placing a calibrated PVDF hydrophone in the test cell. The active area of the hydrophone was 1 mm^2. The results of this measurement are shown in Fig. 7 along with the predictions from Eq. (5). The measured pressure wave agrees only reasonably well with theory.

CONCLUSIONS

The effects of input energy, coefficient of thermal expansion, optical absorption coefficient, and propagation distance on optoacoustic amplitude have been compared to the theory developed by Lai and Young.[13] The experimental observations agree reasonably well with theory suggesting that the principle conversion process is, indeed, dominated by thermal expansion. The absolute magnitude of the optoacoustic signal also compares well to theory.

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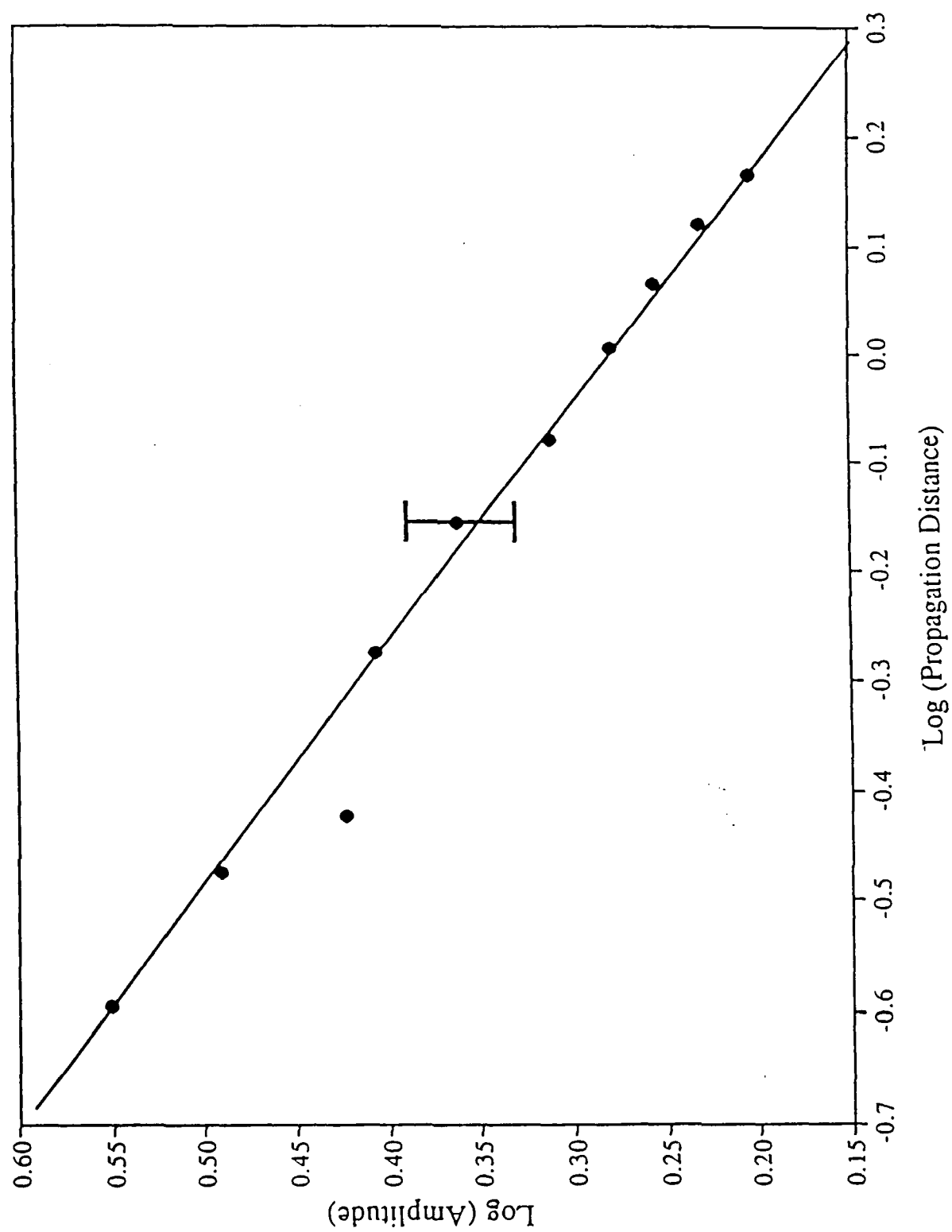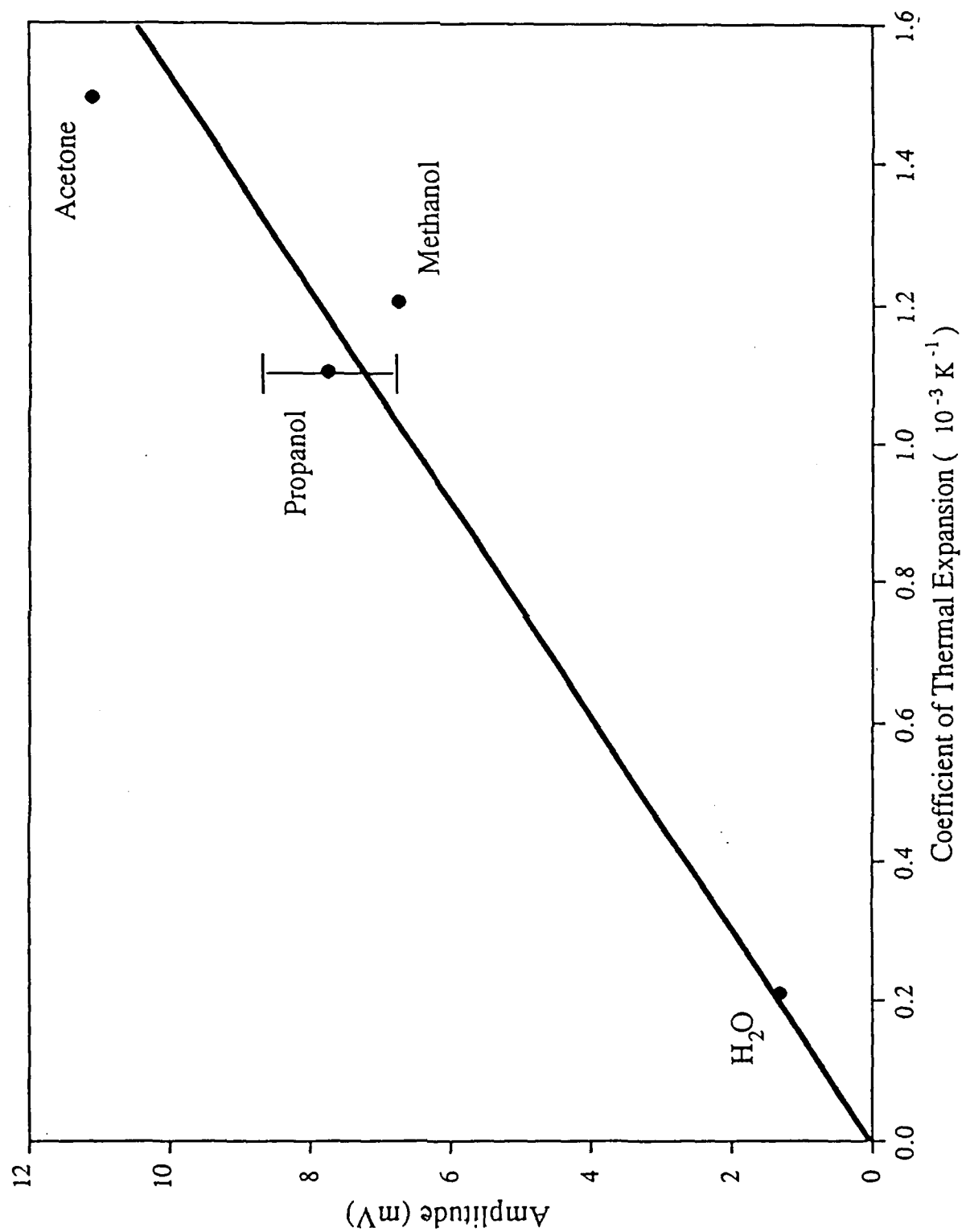
LIST OF FIGURES

M1

Test cell

Trigger Photodiode

Probe Laser

Signal Photodiode

1.3 MW Nitrogen Laser

337 nm Wavelength

800 ps Pulse Duration

oscilloscope

Micro computer

Amplifier

Number of Slides (.23mm/slide)

Energy (µJ)

Log (Propagation Distance)

Log (Amplitude)

33

Signal Amplitude (mV) vs Absorption Coefficient (cm^{-1})
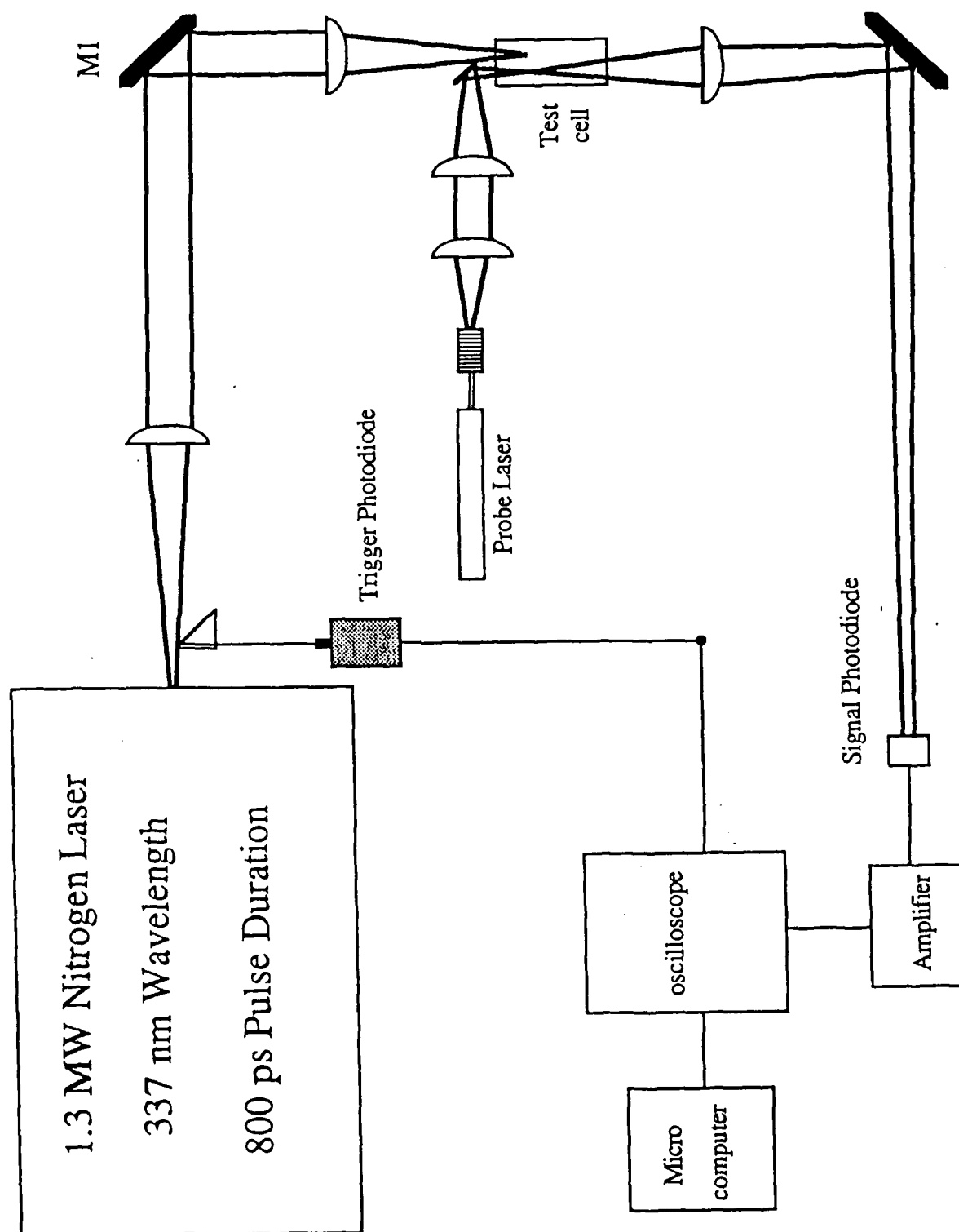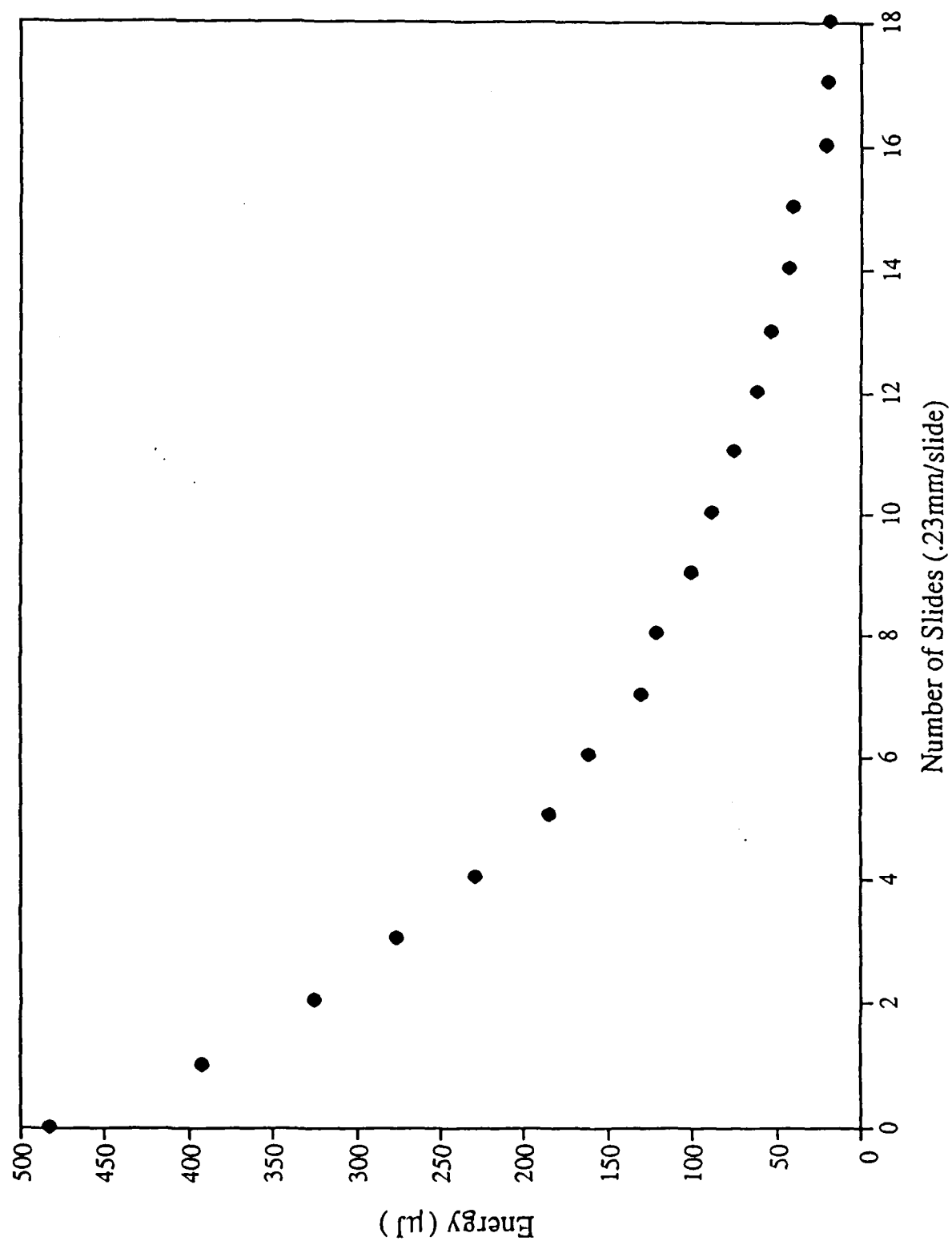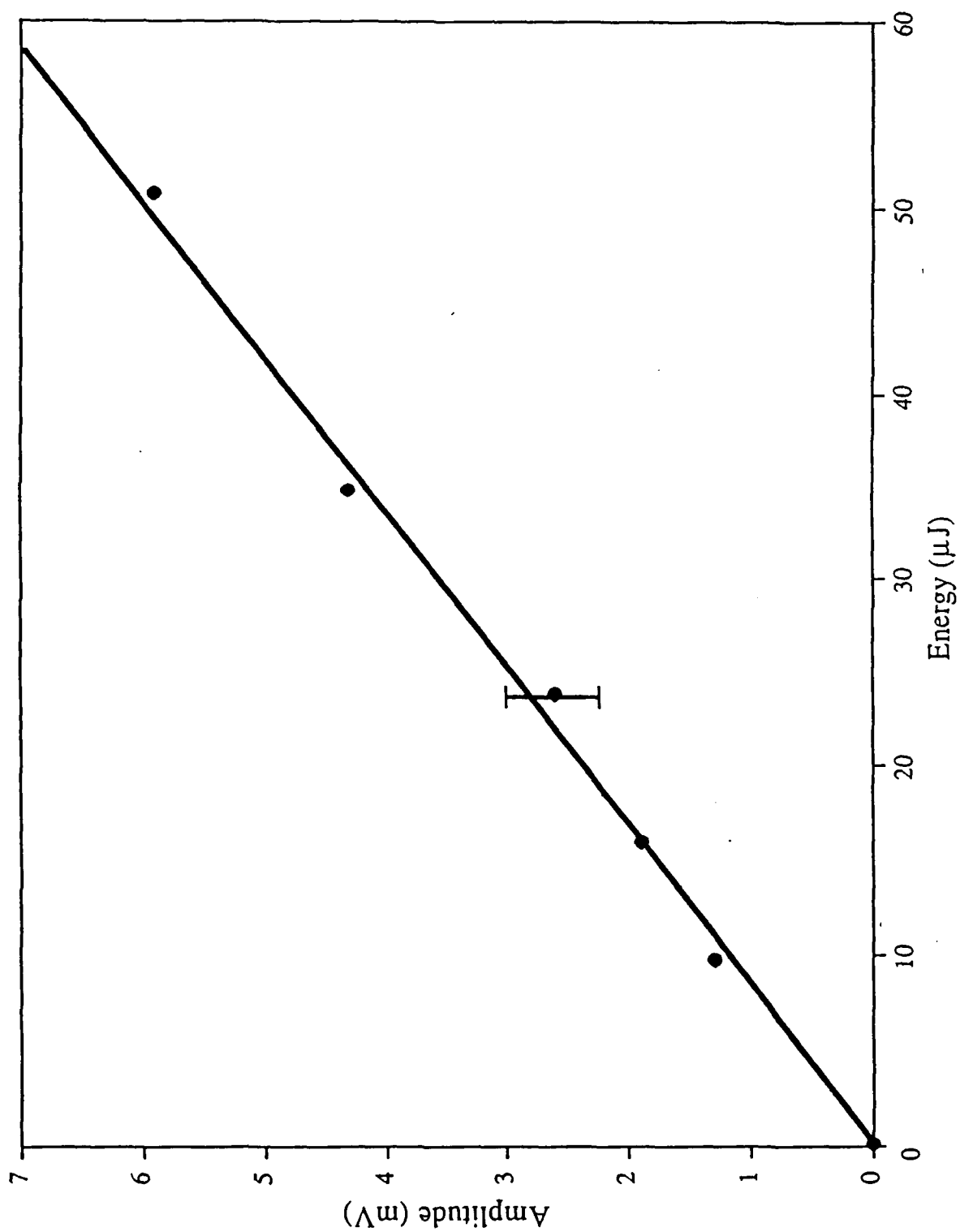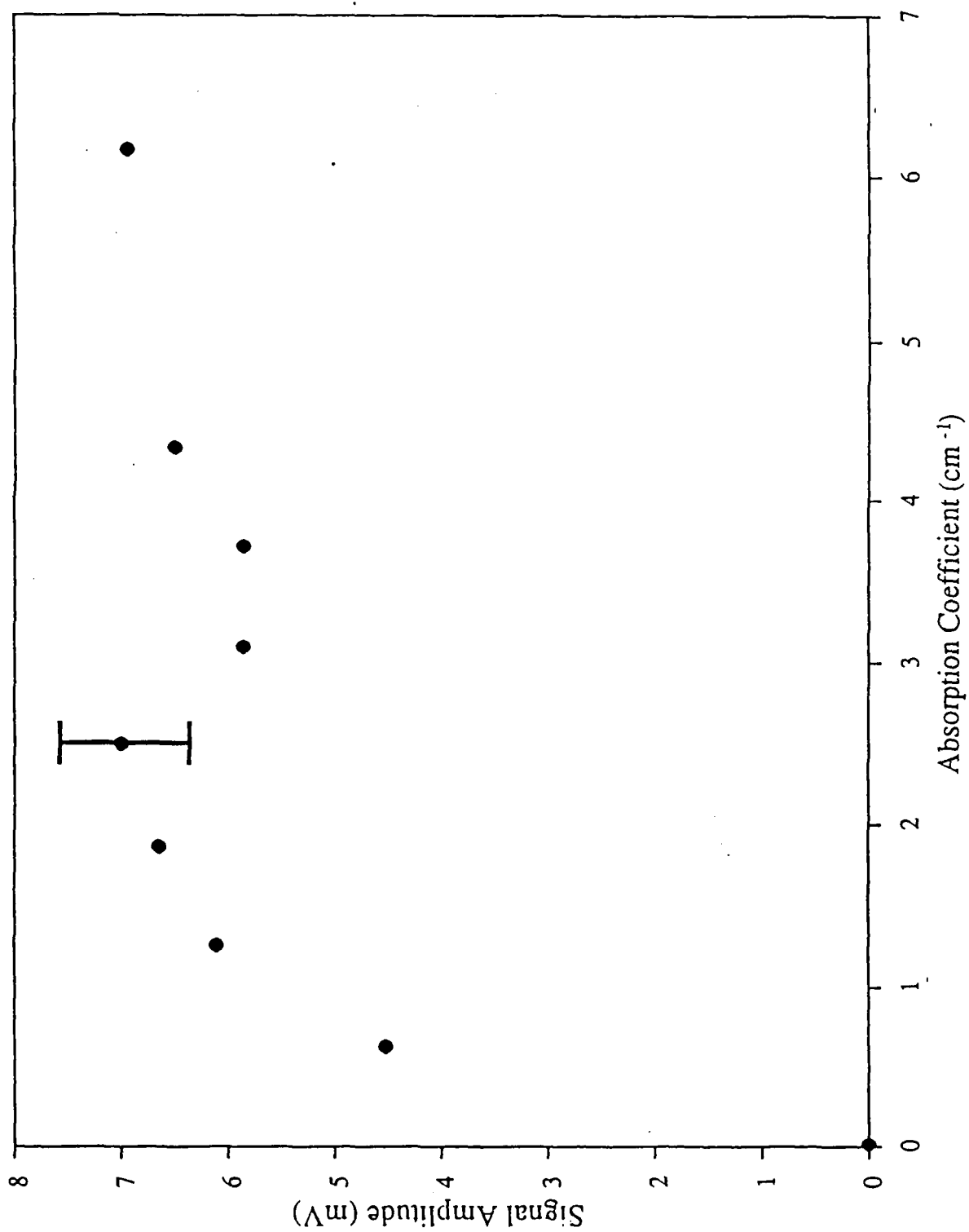
APPENDIX B

OBSERVATION OF OPTOACOUSTIC AMPLITUDE
IN CS$_2$ AT HIGH INPUT ENERGIES

by

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ABSTRACT

The optoacoustic amplitude as a function of laser pulse energy has been measured. A nitrogen laser emitting UV (337 nm) pulses 800 ps in duration was used to excite liquid Carbon Disulfide (CS$_2$), which strongly absorbs the UV radiation. Measurements indicate an optical absorption coefficient of 370 cm^{-1} implying an optical penetration depth of 27 μm. The spatial profile of the pulse was an ellipse at the focal point with dimensions of 330 μm × 90 μm. The energy coupled with the short penetration depth resulted in a high energy density (532 J/cm^3). This was varied by placing glass microslides in the beampath. The optoacoustic amplitude as a function of energy exhibited changes in slope as the liquid in the focal volume underwent vaporization. The experimental observations were explained in terms of an energy dependent coefficient of thermal expansion and optical absorption.

INTRODUCTION

The absorption of a pulse of electromagnetic radiation in a liquid causes density variations which lead to the production of acoustic waves. This phenomena has been observed with X-ray,[1] UV,[2] visible,[3] and IR[4] sources. The principle quantity that differentiates these forms of radiation is their photon energy which dictates the internal state excited. For example, UV and X-rays excite electronic states while infrared radiation excites vibrational states of the molecule. The theory of optoacoustics based upon thermal expansion as the principle generation mechanism makes no distinction between electromagnetic wavelengths except in the optical absorption coefficient, α, which is

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frequency dependent. The fact that the optoacoustic signal agrees well with theory for different wavelengths suggests this is a valid approach.

In this study, we were interested in depositing sufficient energy into a small volume of liquid to result in vaporization. Prior literature suggested that vaporization in itself would provide enhanced optoacoustic amplitude.[5,6] These measurements were made, primarily, in the IR; but based upon linear results, the difference in excitation wavelength probably makes no difference on a time scale long compared to a microscopic interaction time (~ femtoseconds).

There were three primary objectives for this investigation. The first was to measure the optoacoustic amplitude as the input energy was increased to the vaporization threshold of the liquid. The second was to give a qualitative argument to explain the experimental observations. The third was to provide a quantitative mathematical description based on macroscopic physical phenomena.

EXPERIMENT

The experimental configuration is patterned after Sullivan and Tam.[3] The principle components consist of two lasers. A pulsed N_2 laser is used as a source, and a continuous wave (cw) laser is used to detect the optoacoustic signal. The experimental system has been described in detail previously.[2] A block diagram of the experimental setup is provided in Fig. 1 for completeness.

Penetration depth determination for CS_2

The optical absorption coefficient of pure CS_2 at 337 nm is large. To measure the absorption coefficient, small amounts of CS_2 were added to propanol which absorbs UV radiation only weakly. The energy, E, passing entirely through the test cell containing the mixture, measured by an energy meter is

$$E = E_0 \exp -[((1-f)\alpha_1 + f\alpha_2)x + a] \qquad (1)$$

37

where

α_1 = absorption coefficient of pure propanol,

α_2 = absorption coefficient of pure CS_2,

a = dimensionless absorption coefficient of the test cell,

f = volume fraction of CS_2 in propanol, and

x = length of test cell (4 cm).

In all cases of interest, f and a are very small so $\alpha_1(1-f)x+a \cong \alpha_1 x$. The quantity $\alpha_1 x$ can by measured by first measuring the energy, E_{max}, in the absence of the test cell and then the energy, E_0, when the test cell full of propanol is placed in the beam path. We then have

$$E_0 = E_{max} \exp(-\alpha_1 x). \tag{2}$$

For our system, E_{max} was found to be 0.36 mJ and E_0 was found to be 0.34 mJ so $\alpha_1 x = 0.066$. We now can write Eq. (1) as

$$E = E_{max} \exp - [(0.066 + f\alpha_2)]x . \tag{3}$$

The total volume, V, of propanol for this experiment was 12 mL. Drops of CS_2 with a volume of 0.01 mL were added to the propanol so that

$$f = N(.01)/12 \tag{4}$$

where N is the number of drops. Energy transmission was measured after each drop. Using this technique α_2 was deduced to be 370 ± 30 cm^{-1} which implies a penetration

depth for pure CS_2 of $27 \pm 2 \ \mu m$.

Determination of the excitation beam size

The size of a high energy laser beam at the focal point can be determined by various techniques. Knowing the diameter of the incoming collimated beam and the f-number of the focusing lens, one can calculate the minimum spot size possible. This is useful only if the laser is operated in a single mode. The beam from the nitrogen laser used was not very clean, making focusing more difficult. As a result, other techniques were adopted to measure the beam size.

The spatial profile of the excitation beam at the focal point is an ellipse. The ratio of the two axes was determined by exposing a photographic emulsion near the focal point. The size of the exposed portion of the film was then measured under a microscope. The measured dimensions for the axes were found to be 150 $\mu m \times$ 550 μm. This does not represent the true dimensions of the beam due to overexposure of the film and difficulties in positioning the film at the focal plane. The technique does give a good indication of the ratio of the two axes which should remain constant.

The time duration of the optoacoustic signal is primarily determined by the shorter dimension of the excitation pulse provided the excited internal states relax rapidly compared to the optoacoustic signal duration. By comparing the experimental waveform to theoretical predictions, one can determine the spatial width of the shorter dimension. Carbon Disulfide is strongly absorbing at 337 nm, but it relaxes slowly[2] so the resulting time dependence of amplitude is not strongly dependent upon beam geometry. A desirable liquid would relax rapidly upon excitation and moderately absorb the UV laser pulse.

The alcohols used have fast relaxation times (indicated by a short duration optoacoustic signal) but small optical absorption coefficients at 337 nm. Dye must be added to get an observable signal. Although the dye increases the signal amplitude, it also increases the fluorescence output raising the possibility of a zone of secondary absorption. A yellow or red alcohol-based fluid would seem to be ideal for this measurement.

39

Measurements with a number of alcohol-based fluids led us to select a clean brand of scotch. It has a fast relaxation time and presents little problem with fluorescence (at least in the visible spectrum), which resulted in the shortest optoacoustic pulse observed. Comparison of the experimental waveform to linear theory based upon thermal expansion is shown in Fig. 2. This theory has proven successful in predicting waveform shapes in experiments where the beam geometry was carefully controlled.[2] The zero-crossing points are determined by the beam diameter. Using this technique we conclude that the dimensions of the excitation beam at the focal point are 90 μm × 330 μm.

EXPERIMENTAL RESULTS

The objective of this investigation was to examine nonlinear phenomena. The liquid chosen for study was Carbon Disulfide. It absorbs ultraviolet radiation quite strongly giving rise to high energy densities. We wanted to see how the peak amplitude of the optoacoustic response varied with laser pulse energy at intermediate and high energy densities. The results of these measurements are shown in Fig. 3. This graph can be separated into three regions.

Region 1: $0 \leq E < 18\ \mu J$,

Region 2: $18\ \mu J \leq E \leq 80\ \mu J$, and

Region 3: $80\ \mu J < E \leq 298\ \mu J$.

In region 1, the optoacoustic amplitude varies linearly with input energy. A transition occurs at $E = 18\ \mu J$ designating the beginning of region 2. In region 2, the amplitude appears to again vary linearly but with a larger slope than in region 1. A second transition occurs at $E = 80\ \mu J$. In region 3, the optoacoustic amplitude varies nonlinearly with input laser pulse energy.

A few experimental observations should be noted. At $E = 50\ \mu J$ vapor bubbles began

to appear. As the excitation energy was increased vaporization became more apparent. From the specific heat[7] and mass of the excitation volume of liquid, the boiling temperature of CS_2 (319 K)[8] should be reached with a laser energy of 18 μJ. This energy appears to coincide with the end of the first region. From this observation, we conclude that the thermal expansion mechanism is dominant in region 1. Since there is an increase in slope in region 2, a different and more efficient conversion mechanism is suggested. Vaporization is an obvious candidate. In region 3, the input energy is well above the vaporization threshold suggesting that this portion of the curve may be dominated by gas phase properties. Comparing region 2 to region 3 it can be seen that the optoacoustic conversion efficiency decreases with further increase in laser pulse energy. This suggests there is an energy density which gives optimum conversion efficiency.

According to the theory developed by Lai and Young,[9] the optoacoustic amplitude is directly proportional to the coefficient of thermal expansion β. The amplitude of the optoacoustic signal for a weakly absorbing, rapidly relaxing fluid is given by

$$A = \frac{\alpha \beta E}{C_p 8 \pi^{1/2}} \left(\frac{c}{r}\right)^{1/2} \tau_c^{-3/2} . \tag{5}$$

CS_2 is neither weakly absorbing or rapidly relaxing but a more comprehensive calculation[2] gives the same dependence on β and E.

For liquid CS_2,[10]

$$\beta = a + 2bT + 3cT^2 \tag{6}$$

where

$a = 1.1398 \times 10^{-3} C^{-1}$,

$b = 1.37065 \times 10^{-6} C^{-2}$, and

$$c = 1.9225 \times 10^{-8} C^{-3}.$$

For an ideal gas,

$$\beta = \frac{1}{T}.$$ (7)

The expansion coefficient for the three regions is then written as

$$\beta_1 = a + 2bT + 3cT,$$ (8)

$$\beta_2 = (1-f)\beta_1 + f\beta_3, \text{ and}$$ (9)

$$\beta_3 = \frac{1}{T}$$ (10)

where f is some weighted fraction of the excitation volume which has been converted to gas. It is assumed that the fraction $f = 0$ for $E = 18$ μJ and increases linearly until $f = 1$ for $E = 80$ μJ. *change in temperature (ΔT) is related to the laser pulse energy (ΔE) by the heat capacity of the liquid, C_p;

$$\Delta T = \frac{\Delta E}{C_p}.$$ (11)

With the use of Eqs. (8) - (11), the thermal expansion coefficient can be determined as a function of laser pulse energy. These values of β can then be substituted in Eq. (5) to determine the optoacoustic amplitude. This process gives the solid line shown in Fig. 4. Note that the temperature dependence of β successfully explains the amplitude variation as a function of E for all but the latter part of region 3. This discrepancy will be discussed later.

The agreement between data and theory gives rise to some physically appealing results. In region 1 the fluid is composed mainly of clusters of molecules. In region 3, the curve can be explained in terms of an ideal gas suggesting that most of the clusters are

broken apart. Region 2 then, must represent a transition regime of vaporization. Recall that for $E = 50 \ \mu J$, vapor bubbles began to form. This corresponds to a value of $f = 0.5$. This suggests that when 50% of the molecules have been dissociated from their clusters, vapor bubbles began to form.

In previous calculations we have assumed that the absorption coefficient determines the length of the excitation region. The decreased efficiency compared to prediction displayed in Fig. 4 suggests that the size of the excitation region may be increased at high energies. In this case, the original excitation region is completely vaporized and cannot absorb further laser energy. As a result, a portion of the laser energy will penetrate deeper into the liquid.

The latent heat of vaporization is the energy required to completely vaporize a particular volume of liquid. For a volume defined as $6.3 \times 10^{-7} \ cm^3$, this corresponded to a laser pulse energy of 278 μJ in this experiment.[11] In this experiment, we achieved a maximum energy of 298 μJ. We propose that the first 278 μJ of energy vaporizes the original excitation volume and any excess energy penetrates deeper in the fluid.

The spatial profile of the excitation beam at the focal point was found to be an ellipse with major and minor axes of 330 μm and 90 μm, respectively. The additional depth of CS_2 which could be vaporized by the 20 μJ of energy is, then, 1.8×10^{-4} cm. This 1.8 μm is a measure of the depth of additional penetration in the fluid. The results of including this added penetration depth in the optoacoustic amplitude calculation are seen in Fig. 5. The improved agreement suggests that the excitation beam is penetrating further into the fluid.

CONCLUSIONS

The amplitude of the optoacoustic signal does not vary linearly with excitation energy after the energy absorbed by the fluid is sufficient to raise the temperature to the boiling point. This nonlinear behavior, however, is readily explained in terms of a very linear

43

phenomena, thermal expansion. From this viewpoint, the transition from fluid to gas represents an orderly progression in the volume fraction of gas. This smooth transition violates a physical intuition that phase changes occur discontinuously. Note that we do not have the large surfaces normally involved in phase transitions.

Our observations are consistent with the cluster model description of the molecular structure of the liquid. As the number of photons are increased, more molecules are stripped from their clusters. Region 2 probably begins when additional molecules are excited before the first molecules or groups of molecules recombine with their cluster or a neighboring one. Also, the optoacoustic conversion efficiency is at a maximum in region 2 and decreases in region 3. From this, we can conclude that vaporization does increase the optoacoustic conversion efficiency as previous authors have suggested but only when a fraction of the fluid mixture is still acting as an ideal liquid. Once the mixture is dominated by the gas, the conversion efficiency will decrease.

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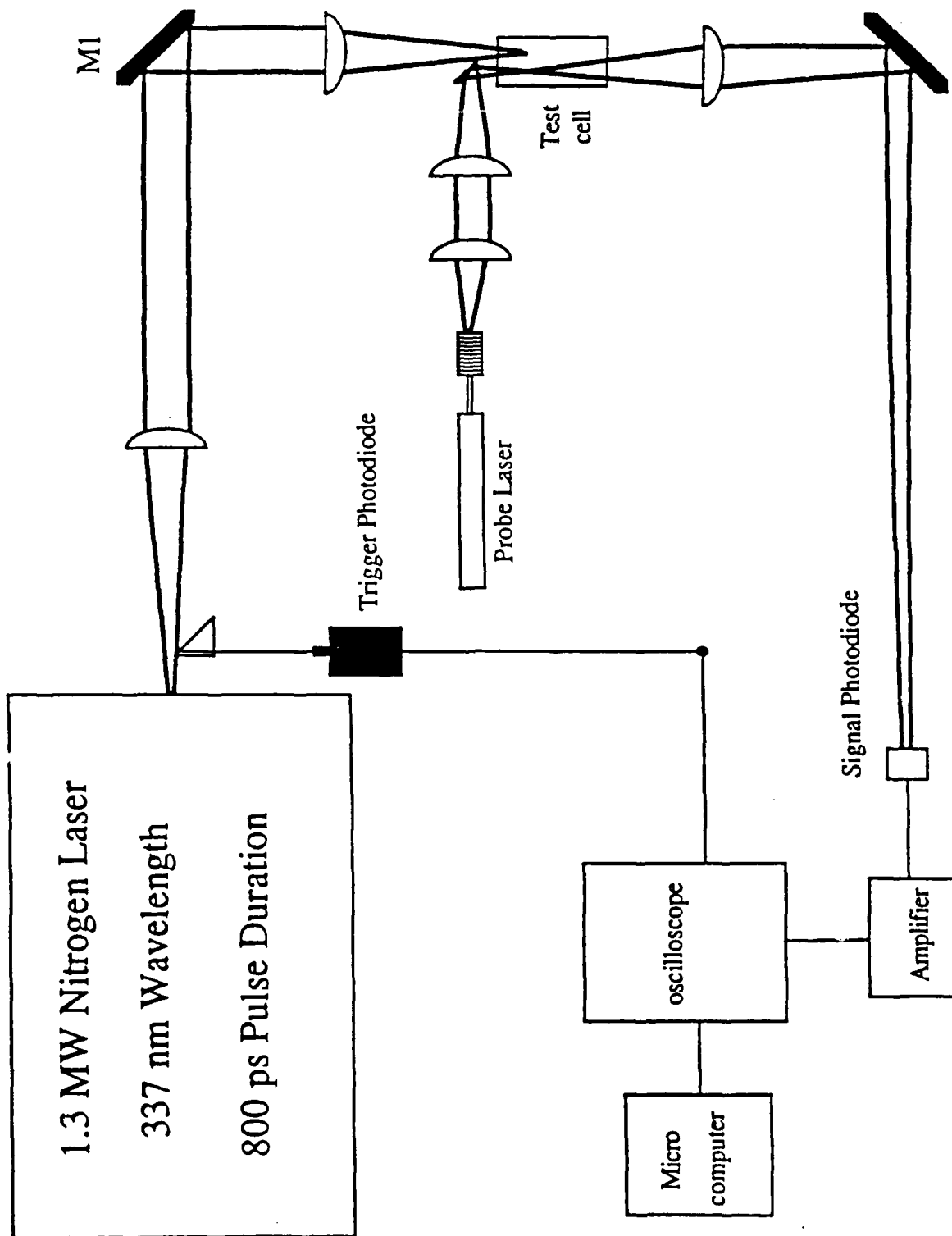
FIG. 1. Variation of translational and vibrational temperature with time for a nitrogen with a small amount of carbon dioxide added as a trace. Shown are the measured translational temperature (■), carbon monoxide vibrational temperature (×), and nitrogen vibrational temperature (+), determined in the manner described in the text. The solid line shows the time dependence of T_v as predicted in ref. 2 from measured values of T assuming a relaxation model explained in the text.
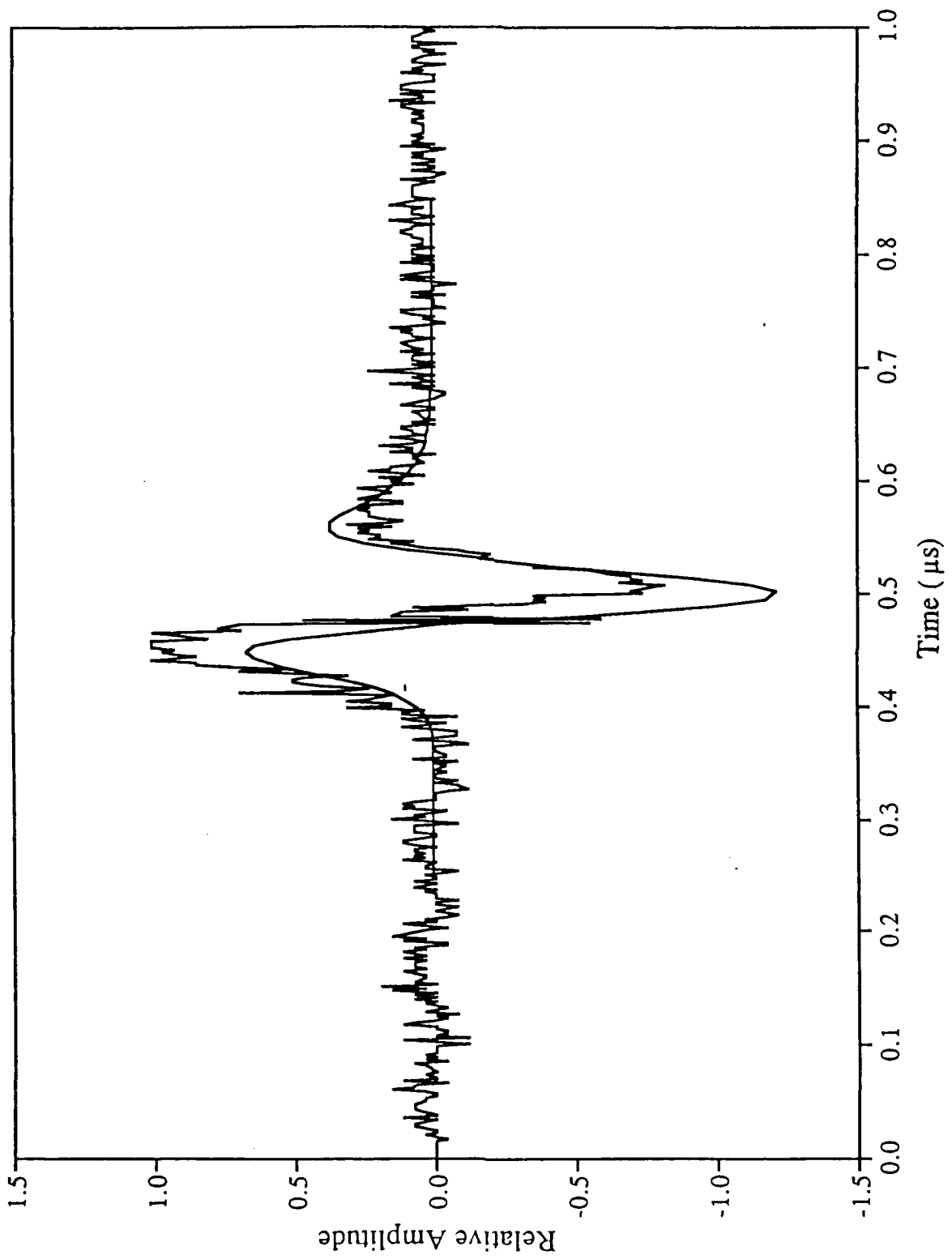
FIG. 2. Variation of translational temperature with time in $H_2/He/CO$ mixtures at various pressures and energies (see Table I). Theoretical curves are calculated for an assumed model as explained in the text.
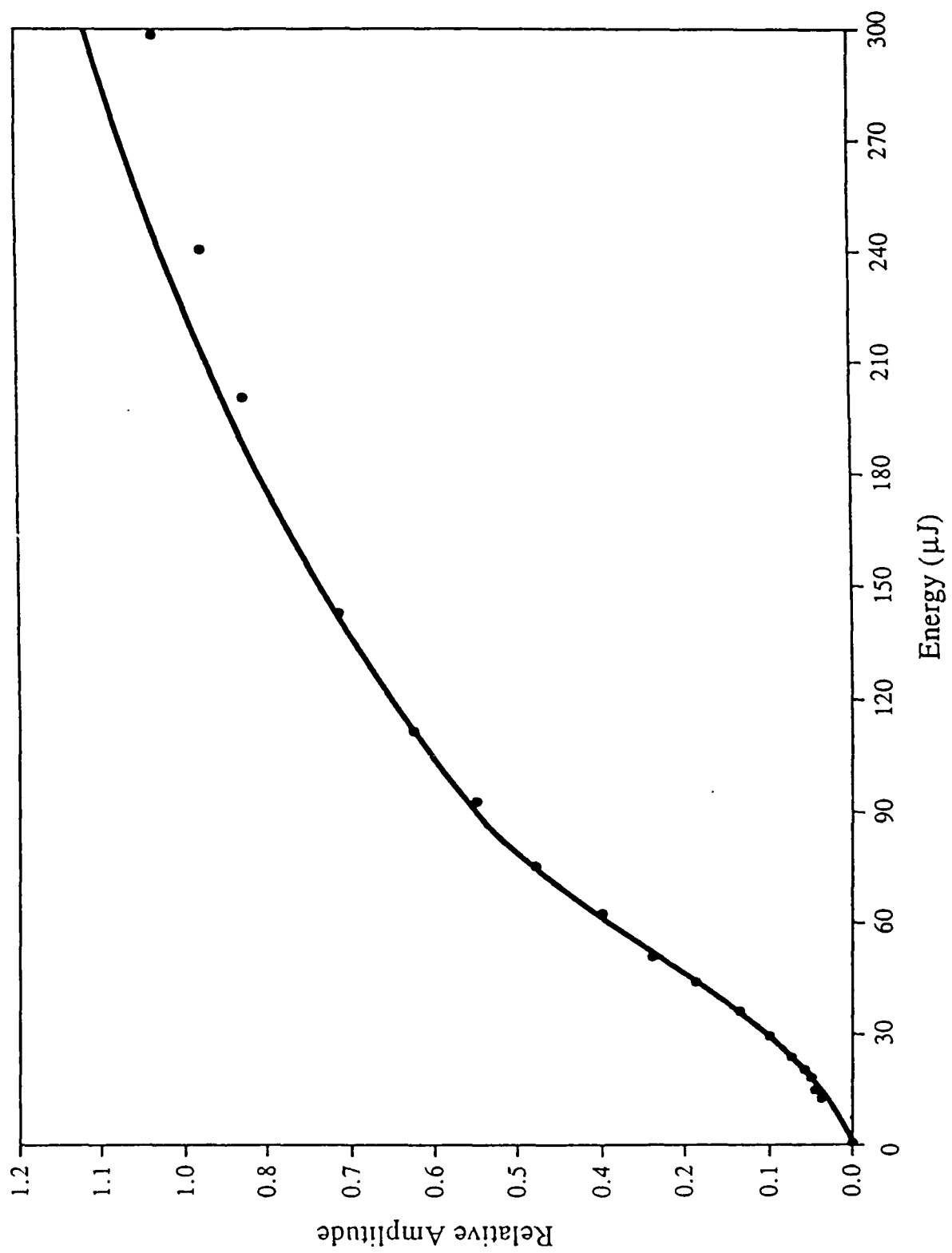
FIG. 3. Variation of sound amplification coefficient for the pulses whose temperature was plotted in Fig. 2 (see Table I). The method for calculating the theoretical curves is given in Ref. 4. In two of the curves, no theoretical fit is shown since it was determined that the relaxation time at some point becomes near to or less than the sound period, violating the condition of a metastable state.

FIG. 4. Relaxation times for a molecule of excited H_2 in an atmosphere of ground state H_2 : – – –, the present work; —, Ref. 10; —. Ref. 11; +, Ref. 12; ◆, Ref. 13; □, Ref. 14.
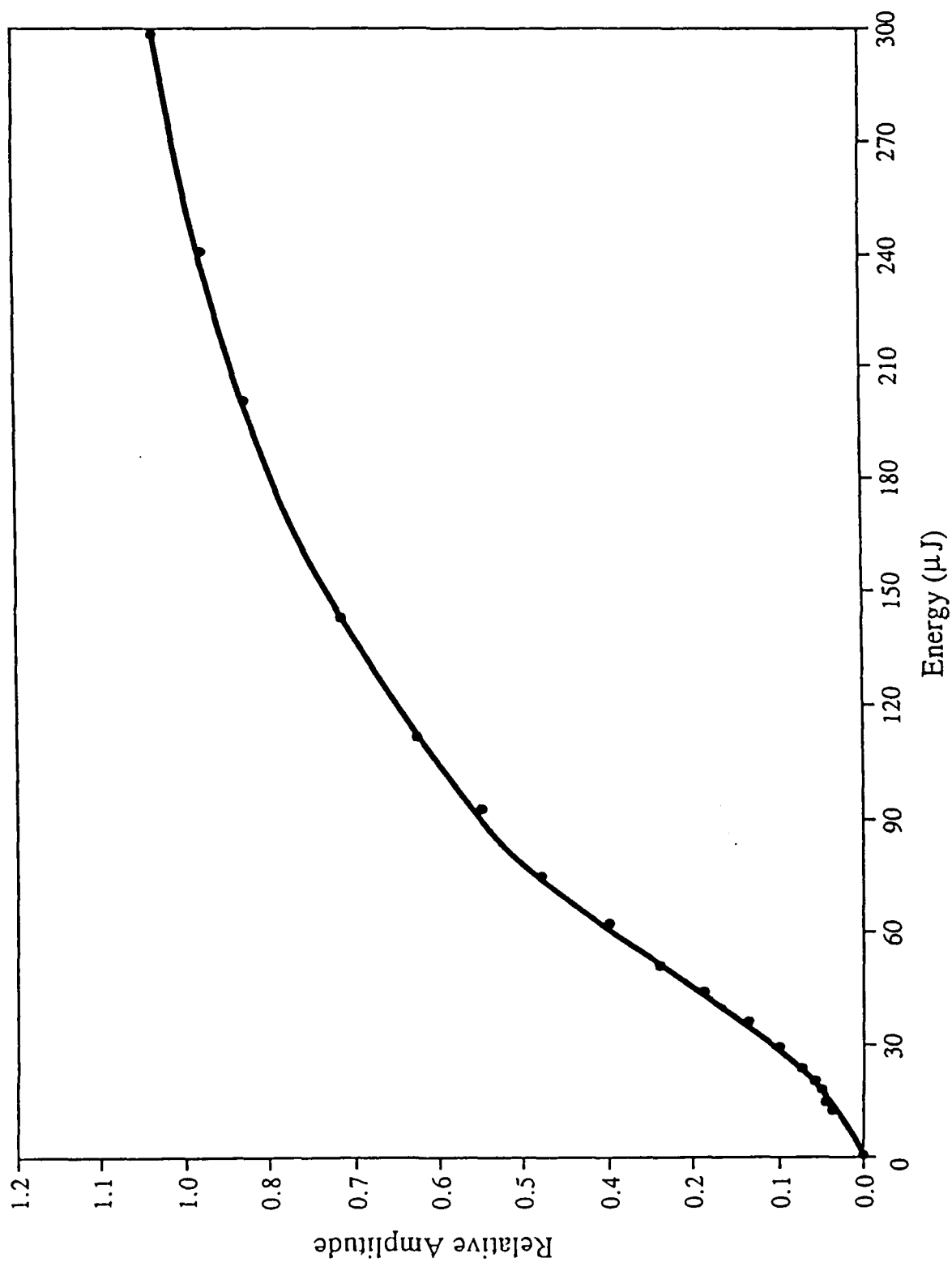
FIG. 5. Relaxation times for a molecule of excited H_2 in an atmosphere of He : – – – , the present work; —, Ref. 10; ◆, Ref. 15.

M1

Test cell

Trigger Photodiode

Probe Laser

Signal Photodiode

1.3 MW Nitrogen Laser

337 nm Wavelength

800 ps Pulse Duration

oscilloscope

Micro computer

Amplifier

Figure showing Relative Amplitude versus Time (μs).

APPENDIX C

Sound propagation in vibrationally excited N_2/CO and H_2/He/CO gas mixtures

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Abstract

Measurements of the resonant reverberation of sound in a tube containing N_2/H_2, N_2/He, N_2/CH_4, and N_2/H_2O mixtures have shown an amplification of the sound following a rapid excitation of the gas by an electric discharge [F. Douglas Shields and L. Dwynn Lafleur, J. Acoust. Soc. Am. **83**, 2186-9 (1988)]. This effect has been named SACER (Sound Amplification from Controlled Excitation Reactions). This paper reports similar measurements in N_2/CO and H_2/He/CO mixtures. It

has been possible in the past to determine vibrational relaxation times and relaxation times for conduction of translational and vibrational energy to the tube walls from the changes in the observed translational temperature of the gas following the electric discharge. In the work reported here, these rates have been confirmed by direct measurement of the decay times of the CO infrared emission.

PACS number: 43.35.Ae

INTRODUCTION

Measurements of the resonant reverberation of sound in a tube containing nitrogen mixed with either hydrogen, helium, methane or water vapor have been performed by Shields[1] and by Shields and Lafleur,[2] in an attempt to observe SACER (Sound Amplification from Controlled Excitation Reactions). They have found gains in excess of those predicted by present theories. This paper reports verification of and extensions to their measurements.

The SACER effect is expected when there is a state of non-equilibrium between the translational and vibrational modes of a gas. This can occur since the vibration-to-translation relaxation time τ_v is often long enough so that a metastable state occurs where the vibrational temper-

ature of the gas may be thousands of degrees higher than its translational temperature. This τ_v is furthermore highly dependent on pressure and temperature, so that a sound wave propagating through the gas may modulate the flow of vibrational energy into translation, allowing for a greater flow during the compressional parts of the sound wave, thereby causing an amplification.[3,4]

EXPERIMENTAL METHOD

Except for one important addition, the experimental method has been described earlier.[1] We excite the vibrational modes of the gas using an electric discharge, and observe the resonant acoustical oscillations within the discharge tube following this discharge with a capacitance microphone mounted in the wall of the tube. From this information, we determine the variation of translational temperature with time following the discharge by observing the variation in frequency of these oscillations. The acoustical amplification is obtained by observing the decay of these oscillations and correcting for viscous, thermal, and end losses. The energy deposited in the gas by the discharge is obtained by measuring the voltage across and the current through the discharge on

a digital oscilloscope, and multiplying the two together.

The additional measurement made in the experiment reported here is the observation of the infrared emission of a small amount of carbon monoxide added to the gas under study to act as a trace of the vibrational energy. This observation was facilitated by the use of a cold gas filter, described by McNair, et al.[5]

The cold gas filter is simply a brass cell terminated by a CaF_2 window on one side and a CaF_2 lens on the other, which can be evacuated or filled to one atmosphere with "cold", that is, room temperature, carbon monoxide gas. Since practically all of the molecules in the cell are in the ground vibrational state, the filled cell acts as a very precise filter of the infrared radiation due to the $1 \rightarrow 0$ vibrational transition of the CO gas in the discharge tube. The filter is interposed between the discharge tube and an InSb infrared detector.

The procedure for using the filter is as follows: Identical discharges are taken with the filter filled and evacuated. If we assume a Boltzmann distribution of harmonic oscillators, then the unfiltered radiation is proportional to the total number of excited CO molecules in the discharge tube, while the filtered radiation is proportional to the number

57

of molecules excited to all levels but the first:

$$\frac{I_{\text{empty}} - I_{\text{full}}}{I_{\text{empty}}} = \left[1 + \frac{1}{\exp(h\nu/k_B T_v) - 1} \right]^{-2}, \tag{1}$$

where I_{empty} is the intensity of infrared radiation passing through the evacuated cold gas filter, I_{full} is that passing through the filled filter, ν is the molecular vibrational frequency of the carbon monoxide, and k_B is the Boltzmann constant. The vibrational temperature T_v of the carbon monoxide in the discharge tube may then be solved for:

$$T_v = \frac{-h\nu}{k_B \ln\left(1 - \sqrt{\frac{I_{\text{empty}} - I_{\text{full}}}{I_{\text{empty}}}}\right)}. \tag{2}$$

To obtain the vibrational temperature of nitrogen in the N_2/CO mixture, we assumed the v-t relaxation in the gas mixture is much slower than the v-v exchange between CO and N_2. (The v-v rate is of the order of 400 $\text{sec}^{-1}\text{torr}^{-1}$ [6-9] while the v-t rate is orders of magnitude smaller[10,11].) In this case, we can assume detailed balancing between vibrational levels in the two gasses.[12] Then

$$k_{j \to (j+1)}^{i \to (i-1)}(a, b) N_i(a) N_j(b) = k_{(j+1) \to j}^{(i-1) \to i}(a, b) N_{i-1}(a) N_{j+1}(b)$$

or

$$\frac{k_{j \to (j+1)}^{i \to (i-1)}(a, b)}{k_{(j+1) \to j}^{(i-1) \to i}(a, b)} = \frac{N_{i-1}(a) N_{j+1}(b)}{N_i(a) N_j(b)} \tag{3}$$

Here, $k^{i \to (i-1)}_{j \to (j+1)}(a, b)$ is the probability that a molecule of gas a in vibrational state i will exchange one quantum of vibrational energy with a molecule of gas b in vibrational state j upon collision. $N_i(a)$ is the number of molecules of gas a in state i, and $N_j(b)$ is the number of molecules of gas b in state j.

The transition probabilities depend only on the translational energy of the particles (and hence, the translational temperature T) and not on their vibrational energy (or vibrational temperature T_a, T_b). Hence, the left side of equation (3) has the same value as it would have if the vibrational and translational temperatures were in equilibrium while the right side corresponds to the populations present in the specified levels when T_a and T_b differ from T and from each other. Therefore, equation (3) becomes

$$\exp\left(\frac{\Delta E(a) - \Delta E(b)}{k_B T}\right) = \exp\left(\frac{\Delta E(a)}{k_B T_a} - \frac{\Delta E(b)}{k_B T_b}\right), \qquad (4)$$

or, for harmonic oscillators of frequencies ν_a and ν_b,

$$\frac{\nu_a}{T_a} - \frac{\nu_b}{T_b} = \frac{\nu_a - \nu_b}{T}. \qquad (5)$$

This equation is used to determine the vibrational temperature of N_2, (T_a), from the translational temperature T (obtained from the sound

velocity measurements) and the vibrational temperature of CO, (T_b), (obtained from cold gas filter measurements).

THEORETICAL PREDICTION OF TEMPERATURES AND GAINS

The following relaxation scheme was assumed to model the flow of vibrational and translational energy to the tube wall:

$$E_{\text{vib}} \xrightarrow{\tau_{vc}} \text{wall}$$

$$\tau_v \downarrow$$

$$E_{\text{trans+rot}} \xrightarrow{\tau_{tc}} \text{wall}$$

In this model, vibrational energy relaxes to the tube wall directly with a relaxation time τ_{vc} and to translation with a relaxation time τ_v. The translational energy then relaxes to the tube wall with a relaxation time τ_{tc}.

The relaxation times for the flow of vibrational and translational energy to the tube wall, τ_{vc} and τ_{tc} respectively, are determined as follows:

The relaxation time for translational energy to the tube wall for a gas in a cylinder whose radius r is much less than its length has been

60

assumed earlier[13,14] to be given by the equation

$$\tau_{tc} = \frac{r^2 C_v \rho}{\left(\pi \beta_{mn}\right)^2 k},$$ (6)

where r is the tube radius, C_v the specific heat of the gas at constant volume, ρ the gas density, and k the gas thermal conductivity. The factor $\pi \beta_{mn}$, the nth zero of the mth order Bessel function, arises from the assumption that the temperature profile is characterized by a Bessel function which goes to zero at the wall of the tube. Assuming a temperature profile characterized by a single zero-order Bessel function whose first zero coincides with the tube wall produces a value of $\pi \beta_{mn} = 2.4$. In order to fit the experimental data, equation (6) was multiplied by a factor of 0.7 for the N_2/CO mixtures (the same factor used in references 1 and 2) and .65 in H_2/CO mixtures. This is justified since the discharge does not fill the tube and the temperature profile in the tube probably does not coincide with a simple zero-order Bessel function.

There have been few measurements of τ_{vc}.[13,16] Shields and Lafleur, however, have developed a theoretical relationship between τ_{vc} and τ_{tc}.[2] Beginning with an energy flux vector developed by Hirschfelder, Curtiss and Bird,[15] and separating out the translational/rotational and vibra-

61

tional parts of the thermal conductivity, they achieve

$$\frac{\tau_{vc}}{\tau_{tc}} = \left(\frac{C_{vib}}{k_{vib}}\right)\left(\frac{k_{tr}}{C_{tr}}\right) = 1 + 2.25\frac{R}{C_{tr}}, \qquad (7)$$

where C_{vib} and C_{tr} are the vibrational and translational/rotational specific heats respectively, and R is the universal gas constant.

The only remaining parameters required to predict the vibrational and translational temperature and acoustical gain of the gas mixture is τ_v and its temperature dependence. This temperature dependence has been written as

$$\tau_v(T) = \left\{\tau_v(T_0)\exp\left[B\left(T^{-1/3} - T_0^{-1/3}\right)\right]\right\}\left(\frac{T_0}{T}\right) \qquad (8)$$

and, therefore, is specified by the value of B. Here T_0 is the temperature of the tube wall.

The procedure for extracting the vibrational relaxation time and its temperature dependence from the experimental measurements is given in previous papers[1,2], and may be summarized as follows:

1. The energy deposited in the gas by the electrical discharge is obtained from the integration of the voltage times the current over the duration of the discharge (about 200 μsec). These voltage and current values are obtained from the digital oscilloscope.

2. The time dependence of the translational and vibrational temperature are extracted from the acoustical and infrared decay curves respectively.

3. The values of $\tau_v(T_0)$, the parameter B in equation (8), and the initial vibrational and translational temperatures are adjusted until the measured decay curves are fit by the relaxation model diagrammed above. In the N_2/CO mixture, all of the discharge energy was assumed to initially go into the vibrational motion of the molecules. The initial translational temperature therefore is room temperature and the initial vibrational temperature is calculated from the measured discharge energy. However, in the $H_2/He/CO$ mixtures the distribution of the discharge energy was found to be more complex. In the 20 torr samples, roughly 5% of the discharge energy was found to be dumped into electronic excitation, and 5–10% into translational modes. In the higher pressure samples, the amount of energy dumped into electronic excitation increased drastically, to as much as nearly 80%. The large amounts of He in the gas mixture makes these observations reasonable. Furthermore,

Shields and Lafleur have reported a similar, though less drastic, loss

of energy to non-vibrational modes in N_2/He mixtures.[2]

The computer program used to carry forth the calculations of step (3)

allows us to predict the translational and vibrational temperatures at

some time t from the initial vibrational and translational temperatures

and the various relaxation times. Since the specific heat and vibra-

tional relaxation times are dependent on temperature, and therefore

on time, the program proceeds iteratively, calculating the specific heat

under the initial conditions, determining from this and the initial relax-

ation times the temperature changes over a time change small compared

to the sound period. Then, new relaxation times are determined, and

the process repeats. The details of the calculations required are given

in references 1 and 2. Values of $\tau_v(T_0)$ and B are varied until the cal-

culated curves of T and T_v vs. time agree with measured values (See

Fig. 2). A single set of $\tau_v(T_0)$ and B values must allow a fit to a whole

set of experimental curves where the pressure and discharge energy are

changed.

EXPERIMENTAL RESULTS

Using these techniques, we attempted to verify the vibrational temperatures for pure nitrogen predicted earlier by Shields and Lafleur.[2] We assumed that the inclusion of a small amount of carbon monoxide did not significantly change the relaxation properties of the gas. Fig. 1 shows our results. The agreement between the theoretically predicted and observed nitrogen vibrational temperature is perhaps most striking in that it confirms the assumed values of both τ_{tc} and τ_{vc} and therefore their ratio. This is experimental confirmation of the ratio τ_{vc}/τ_{tc} theoretically predicted by Shields and Lafleur and given in equation (7).

We then turned our attention to hydrogen. It was soon determined, however, that hydrogen's relaxation time was much shorter than that of nitrogen. In an attempt to slow the relaxation, helium was added to the mixture. Discharges were made at several pressures and energies, and the assumed values of $\tau_v(T_0)$ and B in equation (8) were adjusted in order to fit the theoretically predicted translational temperatures to the measured values (see Fig. 2 and Table 1), allowing us to determine the vibrational relaxation time as a function of temperature.

The predicted amplification (SACER) was also compared to the observed gain corrected for viscous, thermal and end losses (Fig. 3). Ref-

65

erence 1 explains these corrections in detail. As can be seen, we have correctly predicted that the amplification should be negligible in the time interval measured.

From the determined values of the relaxation times in the "pure" H_2 and those of the H_2/He system, we can determine the vibrational relaxation times of H_2 in collisions with itself ($\tau_{H_2-H_2}$), and in collisions with He (τ_{H_2-He}). Again, we assume that the presence of carbon monoxide makes no significant contribution to the relaxation. Figs. 4 and 5 show a comparison of these results with those of earlier investigators. In addition to our results, Fig. 4 shows two high-temperature shock-tube measurements[17,18] and three room-temperature or low-temperature Raman spectroscopy measurements[19,20,21] for $\tau_{H_2-H_2}$, and Fig. 5 shows one high-temperature measurement[17] and one room-temperature measurement[22] for τ_{H_2-He}. The room-temperature values we determined are about an order of magnitude less than those previously determined, and our measured temperature dependence is greater than that implied by others.

In summary then, we have determined approximate values of the relaxation times for hydrogen in collisions with itself and with helium. The times we have observed are an order of magnitude smaller than those

measured by other investigators at room temperature and have a greater negative temperature dependence. Because the relaxation occurs so rapidly in H_2, the SACER effect is difficult to observe in this experiment. However, most notably, we have confirmed relaxation times for the conduction of both translational and vibrational energy to the tube wall in N_2, verifying the equation for the ratio of these times developed by Shields and Lafleur.

ACKNOWLEDGMENT

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TABLE I. Parameters for the gas mixtures plotted in Fig. 2 and Fig. 3.

Graph	Mixture	Pressure (Torr)	Energy (J/mole of H_2)
A	99% H_2/1% CO	27	5030
B	52.6% H_2/46.7% He/0.7% CO	20	4930
C	52.6% H_2/46.7% He/0.7% CO	20	7620
D	52.6% H_2/46.7% He/0.7% CO	40	5010
E	52.6% H_2/46.7% He/0.7% CO	80	4450

LIST OF FIGURES

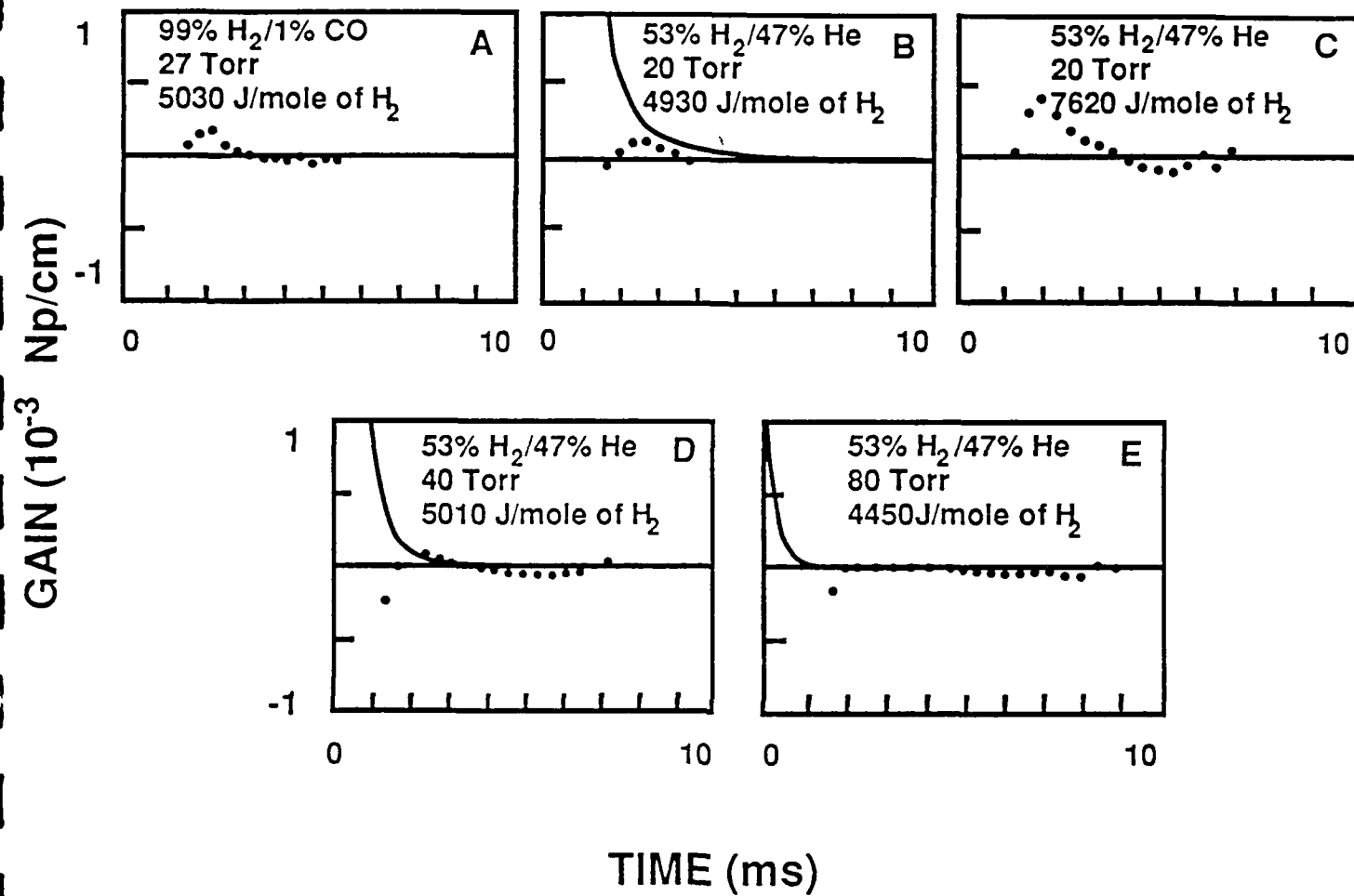Figure 1
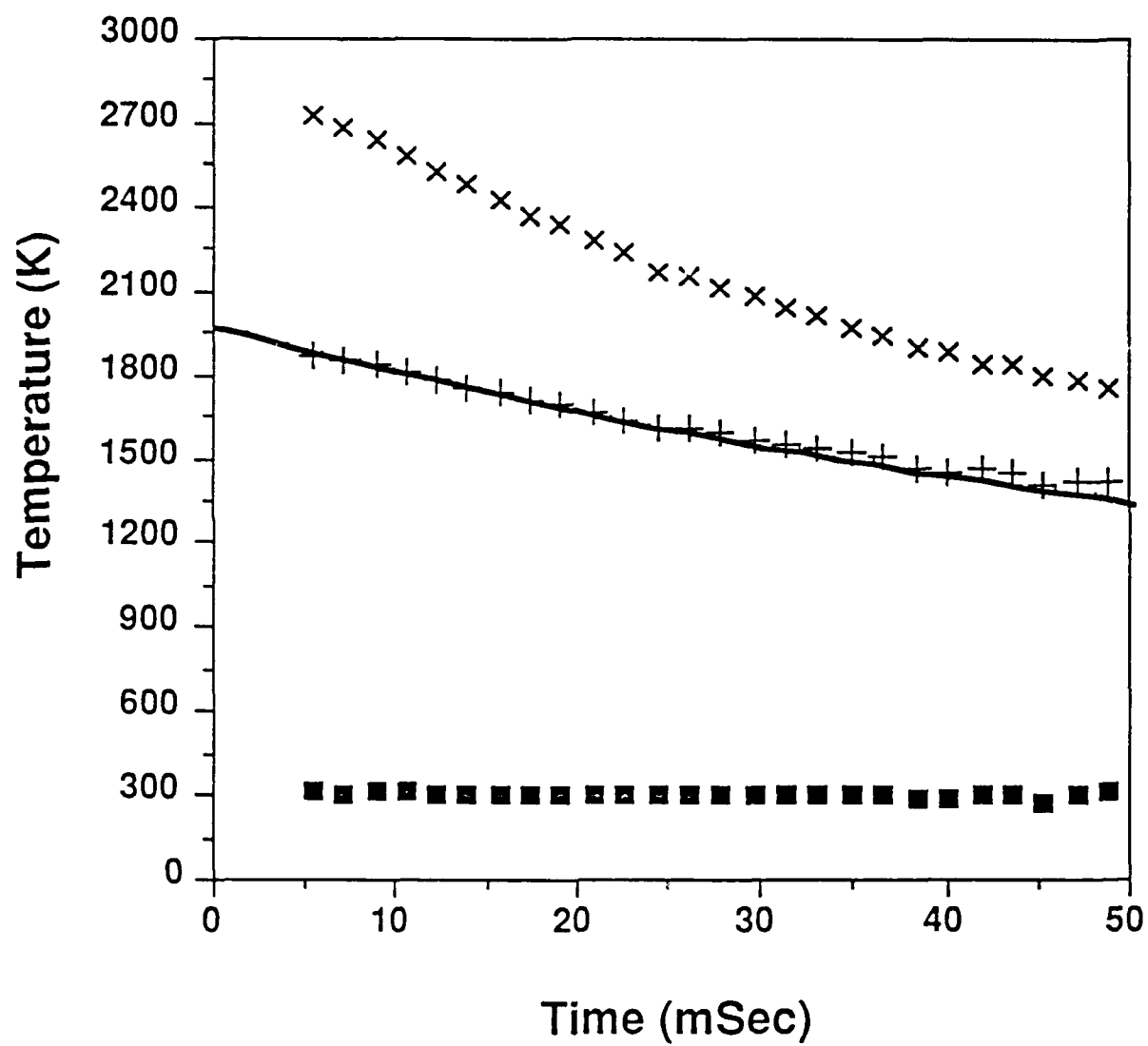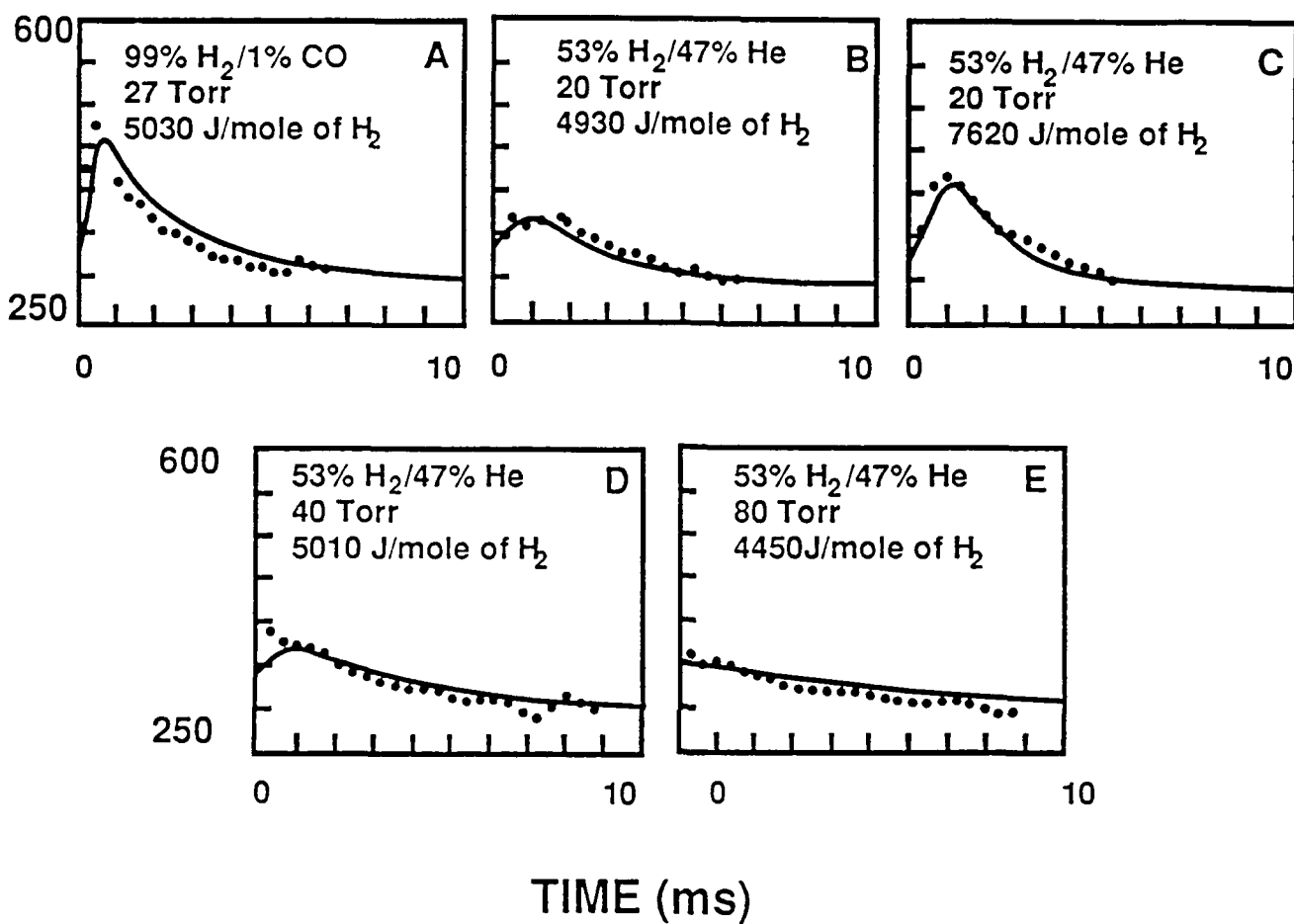
Figure 2

Figure 3

Figure 4

Figure 5

76
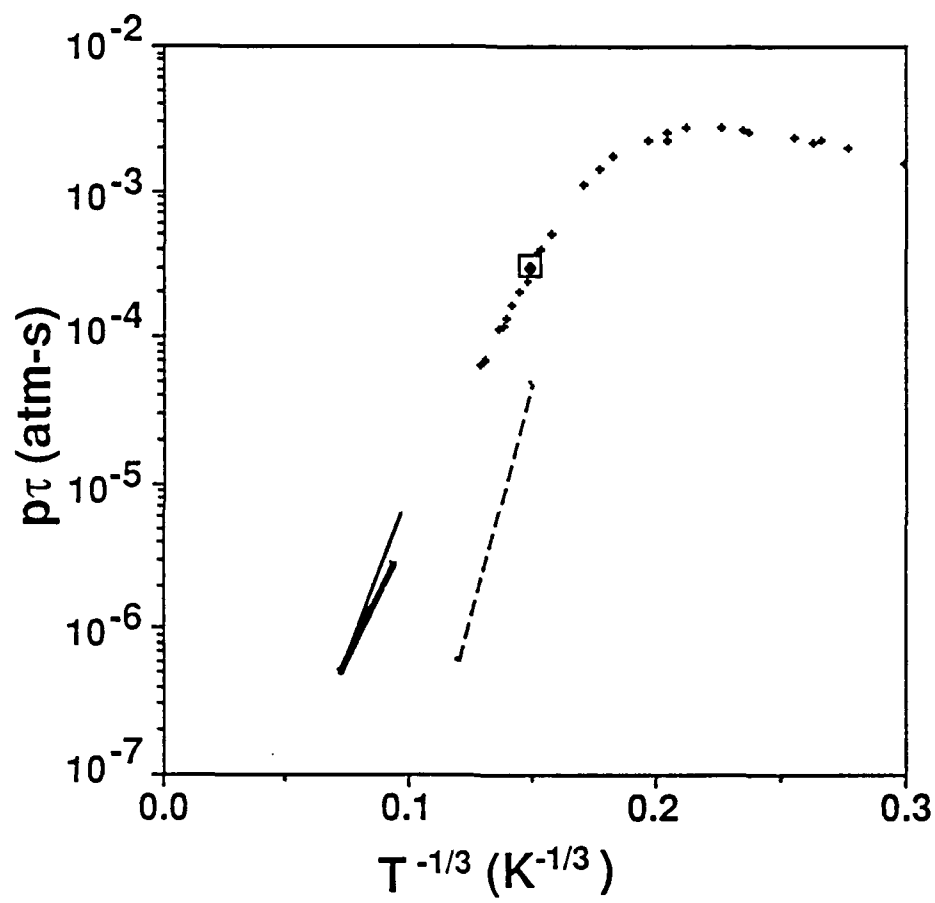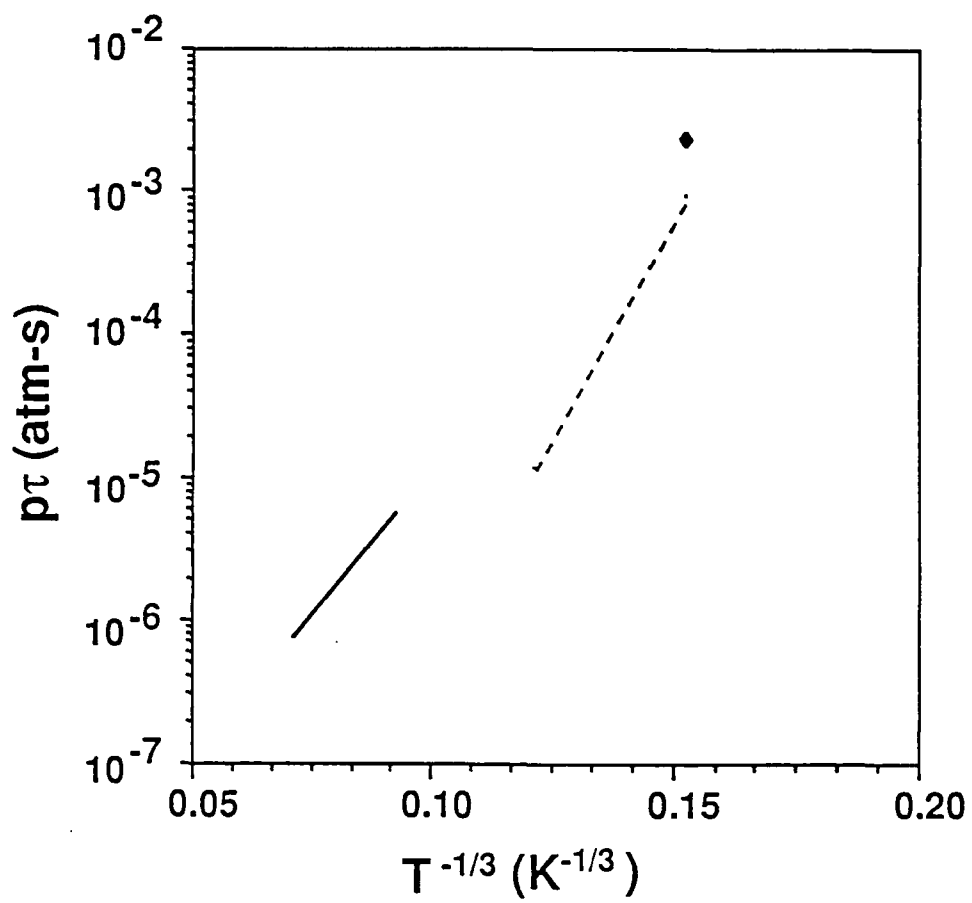
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